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THE REACTIONS OF ACTIVE NITROGEN WITH ETHYLENE
AND DEUTERATED ETHYLENES

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

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UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled THE REACTIONS OF ACTIVE NITROGEN WITH ETHYLENE AND DEUTERATED ETHYLENES submitted by Kenneth Dey Foster, B.Sc., in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

The reactions of active nitrogen with C_2H_4 , C_2D_4 and C_2D_3H have been studied in a fast flow system at total pressures of 0.6 and 2.6 Torr.

Atomic nitrogen concentration measurements throughout this work were made with an MS 10 Mass Spectrometer (Associated Electrical Industries) which was suitably modified for nitrogen atom detection.

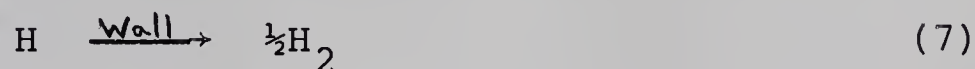
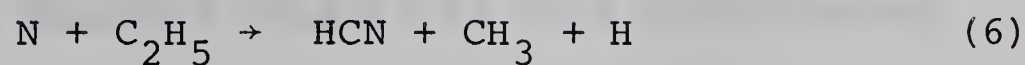
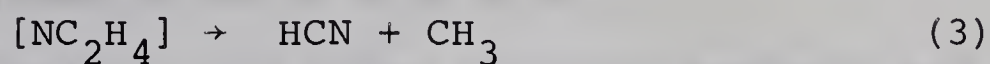
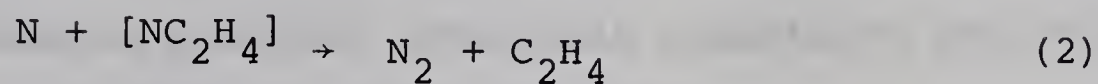
The apparent second order rate constant for the reaction of nitrogen atoms with ethylene was determined to be $(3 \pm 1) \times 10^{-13}$ cc molecules⁻¹sec⁻¹.

Experiments with "poisoned" and "unpoisoned" systems showed that there were more nitrogen atoms destroyed and ethylene molecules destroyed in the "poisoned" system than in the "unpoisoned" system, at low rates of ethylene input.

The use of a separate discharge, through which hydrogen was passed, enabled measurement of the effect of hydrogen atom addition on the reaction of nitrogen atoms with ethylene. Enhancement of the amount of HCN produced from the reaction was observed, in agreement with the results of experiments conducted by Herron,⁴⁰ in which molecular nitrogen and hydrogen were premixed before passing through a discharge.

The ratio of nitrogen atoms destroyed to ethylene molecules destroyed was found to decrease with increasing initial ethylene input rate, and with decreasing initial nitrogen atom concentration.

A mechanism which appears to be consistent with these results is



The experimental data provide conclusive evidence that the maximal yield of HCN from the reaction of active nitrogen with ethylene does not give an accurate measure of the nitrogen atom concentration in active nitrogen.

ACKNOWLEDGEMENTS

The guidance and support throughout this work of Dr. H.B. Dunford, the project supervisor, is gratefully acknowledged.

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INTRODUCTION

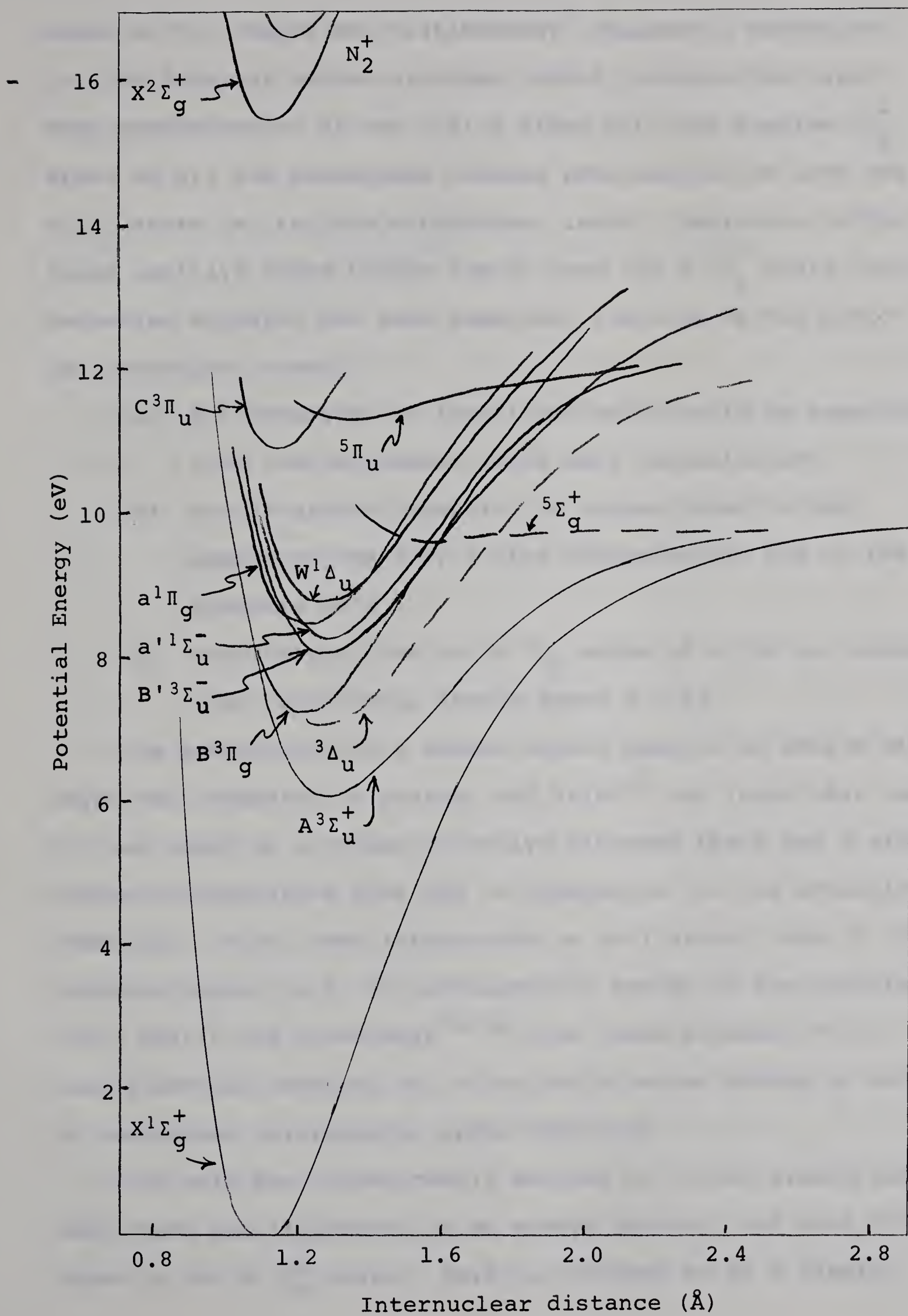
THE NATURE OF ACTIVE NITROGEN

Nitrogen, which is normally quite inert, takes on different properties when subjected to a sudden energy perturbation, such as a d.c. condensed discharge or an electrodeless discharge. In either case the nitrogen exhibits a so-called afterglow, which may persist for several seconds after the discharge has been turned off. This glow is generally yellow-orange in color and is sometimes referred to as the Lewis-Rayleigh afterglow.^{1,2} Active nitrogen is given this name primarily because of its high chemical reactivity. For the last half century active nitrogen has been the subject of investigations by physicists and chemists alike. Several of these studies have been summarized and reviewed in the literature.^{3,4,5} Various theories have been put forth to explain the phenomenon. Both excited atoms⁶ and ionic species³ have been suggested as the important energy carriers. However, these have both been abandoned as possible candidates, primarily on the grounds that they are not present in high enough concentrations. (⁴S) N atoms are now known to be the predominant species in nitrogen exhibiting the normal Lewis-Rayleigh afterglow.^{8,9}

The Lewis-Rayleigh afterglow is primarily due to transitions from the 12th, 11th, 10th, and 6th vibrational levels of the B $^3\Pi_g$ state of N₂ to the A $^3\Sigma_u^+$ state of N₂, as shown in Fig.1. These transitions are known as the first positive

Figure 1

Potential Energy Curves for Molecular Nitrogen



bands of N_2 . Bayes and Kistiakowsky⁷ proposed a mechanism for the decay of active nitrogen, which involves the three body recombination of two (4S) N atoms into the shallow $^5\Sigma_g^+$ state of N_2 , and subsequent inverse predissociation into the B $^3\Pi_g$ state in its 12th vibrational level. Radiation of the first positive bands brings the N_2 into its A $^3\Sigma_u^+$ state. This mechanism explains the most important features of the nitrogen afterglow, namely

- (a) the afterglow is long-lived which would be expected from the improbable three body recombination.
- (b) the afterglow intensity is proportional to the square of the (4S) N atom concentration and to the pressure of N_2 .
- (c) transitions from the B $^3\Pi_g$ state of N_2 do not occur from vibrational levels above $v = 12$.

The possibility of a second active species in active nitrogen was suggested by Kaufman and Kelso¹⁰ who found that when N_2O was added to a stream of active nitrogen there was a significant temperature rise and a diminution of the afterglow intensity. This, they interpreted as collisional loss of vibrational energy in N_2 to translational energy of the polyatomic N_2O . Schiff and co-workers^{11,12} also found evidence for a second species carrying ca. 6 kcal/mole excess energy, by using an isothermal calorimetric probe technique.

Not only has vibrationally excited N_2 in its ground electronic state been suggested as an energy carrier, but also nitrogen in its A $^3\Sigma_u^+$ state. This is believed to be a likely

candidate since it is the first electronically excited state, and it is the product of the Lewis-Rayleigh afterglow. Its radiative decay is forbidden on the basis of spin conservation, thus allowing the possibility of a sufficiently long life to undergo chemical reaction. Lifetimes in the ranges 0.026 sec to 0.1 sec^{13,14,15} and 0.9 to 2.0 sec^{16,17} have been suggested for the A state of N₂. It has been suggested by Dunford and co-workers¹⁸ that differences in the published lifetimes of the A state lie in the distinction between true radiative lifetimes and collisional lifetimes. A collisional lifetime would be calculated on the basis of pseudo-first order reaction reaction such as $N_2^* + M \rightarrow N_2 + M$ for a given M concentration. They noted that, if in fact a collisional lifetime has been measured, the nature of M is still undetermined. It need not be N₂ but perhaps O₂ impurity or even Hg. Also M may be associated with the surface or something adsorbed on the surface.

Metastable states of atomic N, i.e. (²D)N and (²P)N have been found to be present but amounted to only ca. 0.2 % of the (⁴S)N concentration.¹⁹

Under certain conditions, pure nitrogen will exhibit a so-called "pink afterglow"²⁰ which is superimposed upon the normal Lewis-Rayleigh afterglow and occurs downstream from the discharge. The normal Lewis-Rayleigh afterglow prevails both upstream and downstream from this pink region. The glow apparently occurs in very pure nitrogen under fast flow conditions at ca. 4 to 7 torr, and is characterized by relatively

high ion densities and excited nitrogen atom densities.²¹ Radiation from the glow shows the second positive ($C^3\Pi_u \rightarrow B^3\Pi_g$) and first positive ($B^3\Pi_g \rightarrow A^3\Sigma_u^+$) bands of N_2 , the first negative bands of N_2^+ , and also atomic emissions.

MONITORING OF SPECIES PRESENT IN ACTIVE NITROGEN

A. Physical Methods

K.R. Jennings gives a comprehensive review of atom detection methods.²² In 1929, Wrede²³ developed a method of measuring absolute atom concentrations in simple systems at low pressures. The apparatus consisted of an orifice leading from the tube, along which the gas was flowing, to a small volume with a catalytic surface. If flow through the orifice is molecular, then a pressure gradient is set up across the orifice due to atom recombination in the catalytic section. The atom content in the system is then found by measuring this pressure difference, ΔP . The time necessary to attain equilibrium varies inversely with the area of the hole and directly with the volume behind the hole.

Another method for measuring absolute atom concentrations was developed by Elias,²⁴ also based on the change in pressure resulting from atom recombination. A steady flow of the partially dissociated stream is established through a test volume which can be quickly isolated. The accuracy of the method is subject to two conditions: (a) that the trapping process is fast with respect to the average lifetime of the atoms and (b) that isothermal conditions prevail such that

$C_A = 2\Delta P/RT$, where C_A = atom concentration and ΔP = pressure loss due to atom recombination.

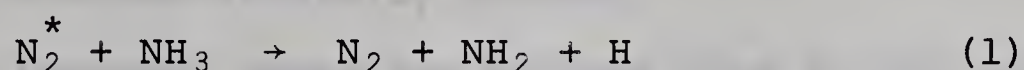
The use of catalytic probes and isothermal calorimeters for N atom detection and measurement has not been widespread. The catalytic probe is designed to remove as few atoms as possible from the gas stream whereas the isothermal calorimeter removes all the atoms from the stream. The methods have been applied to O atoms however,²⁵ and to H atoms.²⁶ These methods have the disadvantage of being very unselective regarding energy carriers, that is, the probe will not only receive the energy resulting from recombining atoms but also from excited molecular or atomic species.

Atomic nitrogen has three unpaired electrons in its ground state. This fact makes its detection and measurement possible from magnetic resonance experiments, and many electron paramagnetic resonance (e.p.r.) experiments have been done on the active nitrogen system.^{27,28,29} This method is quantitative, its sensitivity is high (measurements of 10^{12} atoms/cc can be made), and the system is not perturbed by the measurements. Also, e.s.r. experiments are not limited to atoms but would in theory measure any species with an unpaired electron.

Mass spectrometers have perhaps been the most widely used physical method and their use will be considered in some detail later.

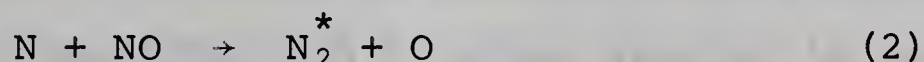
B. Chemical Methods

Ammonia has been found to have no effect on the N atom concentration when added to active nitrogen.³⁰ However, NH_3 destruction by active nitrogen produced in a condensed discharge, is found to increase with increasing NH_3 input rate until it reaches a constant value independent of NH_3 input. For this reason, it has been suggested that NH_3 is destroyed by molecular N_2 in its $\text{A}^3\Sigma_u^+$ state.³¹ The first step of this decomposition is believed to be



The extent of NH_3 destruction has been used as a direct measurement of the $\text{A}^3\Sigma_u^+$ N_2 concentration by Dunford.¹⁴

Ozone has been used by Schiff and co-workers³² to measure the concentration of vibrationally excited N_2 resulting from the reaction



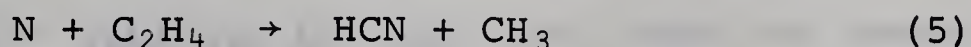
Nitrogen atoms have been determined chemically in two different ways. The first method utilized the reaction of N atoms with nitric oxide as a titration technique. This involves the coexistence of reaction (2) with the reactions



The visual end-point occurs when the N and NO flow rates are equal. Then reaction (2) predominates and there is no fluorescence.

Another method for determining the N atom concentration,

which has been utilized by Winkler and co-workers,^{33,34,35} is based upon the maximum yield of HCN from the reaction of active nitrogen and ethylene. This reaction has been postulated to proceed by the mechanism



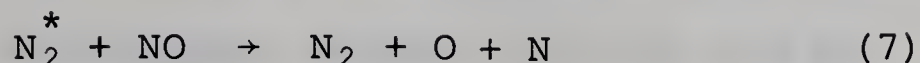
followed by the fast consumption of N atoms by



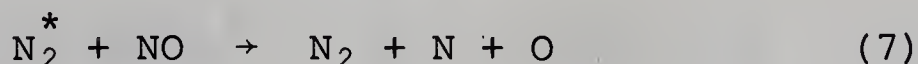
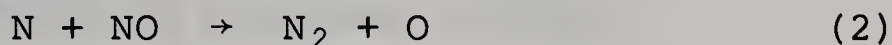
such that a measure of the maximum HCN produced is a measure of the amount of N atoms initially present.

In general, however, these two methods give N atom concentrations which do not agree, the NO method giving a value ca. 1.5 times larger than HCN, depending on the conditions. Verbeke and Winkler³⁶ found the ratio of [N] determined from the NO titration to [N] determined from HCN yield, i.e. $\Delta\text{NO}/\text{HCN}$, increased with increasing N_2 pressure, and suggest that NO is capable of reacting with a second species in active nitrogen. They favor the $\text{A}^3\Sigma_u^+$ state of N_2 since the dissociation limit of NO is near the excitation energy of $\text{A}^3\Sigma_u^+$ over the ground state. These authors favor the HCN scheme because the "...maximal HCN production is found to be essentially the same as that from such diverse reactants as propane, isobutane, cyclopentane..." They reject the idea of a catalyzed recombination of N atoms by substrate³⁵ on the basis that the "plateau from which the active nitrogen concentration is inferred in the C_2H_4 reaction is not dependent upon either the flow or the temperature."

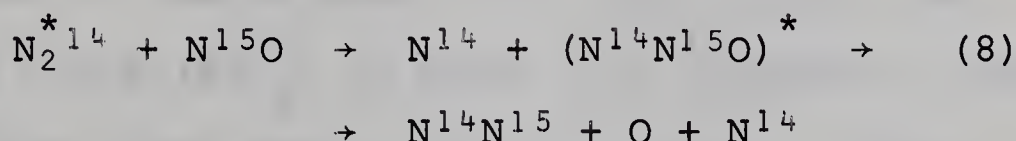
Back and Mui,³⁷ in an attempt to show the existence of the reaction



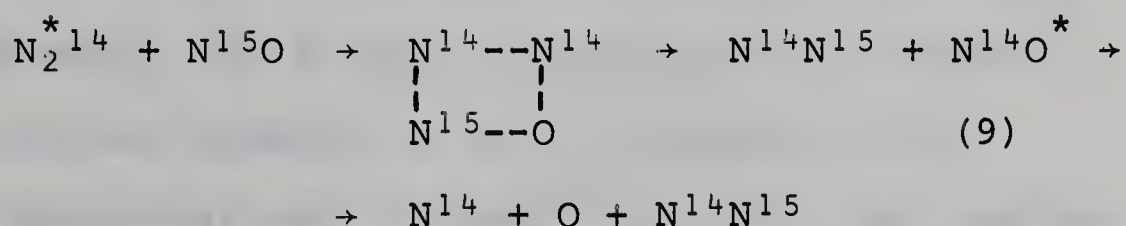
postulated by Verbeke and Winkler, where N_2^* is N_2 in the $\text{A}^3\Sigma_u^+$ state, used N^{15} labelled NO such that from the competing reactions



there would be some detectable N_2^{15} produced from atom recombination if reaction (7) were occurring and only $\text{N}^{14}\text{N}^{15}$ if reaction (2) were the only important reaction. However, it was found that the N^{15}O was consumed quantitatively by active nitrogen to produce only $\text{N}^{14}\text{N}^{15}$ with almost no N_2^{15} being formed. This then, invalidated the proposed consumption of NO by the reaction (7). However, these authors do note the possibility of a reaction scheme such as



or perhaps a four center reaction such as



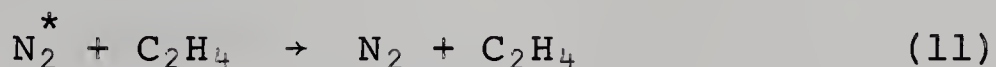
Both of these processes could proceed without the formation of N_2^{15} .

In the above experiments, the $\text{N}^{14}\text{N}^{15}$ yield was equal to the amount of NO destroyed. Back and Fersht³⁸ therefore

deduced that since HCN and $N^{14}N^{15}$ would probably not undergo secondary reactions, the study of these products might give more insight into the discrepancy between the C_2H_4 and NO reactions. This prompted them to study the reaction of active nitrogen with mixtures of C_2H_4 and $N^{15}O$. Their results are shown in Fig.2. Back explains this behaviour on the basis that NO also reacts with N_2^* in a process such as



He states that, as small amounts of C_2H_4 are added to an excess of $N^{15}O$, the C_2H_4 competes with NO for N_2^* but does not undergo chemical reaction, i.e.,



this process being five to ten times faster than the reaction of NO with N_2^* . According to Back, these data then represent two distinctive competitions of C_2H_4 and NO for reactants: one for N atoms in which NO reacts about 100 times faster than C_2H_4 and the other for $N_2(A^3\Sigma_u^+)$ in which C_2H_4 quenches A state molecules five to ten times faster than NO reacts. These workers therefore favored the HCN method for measuring N atom concentrations. However, the N atom concentration as determined by the NO titration appears to be in agreement with e.s.r. results of Westenberg and de Haas²⁸ and with the results of Elias.²⁴ In Back's system, there is the possibility of complicating reactions such as

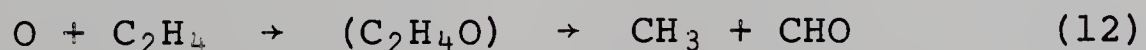
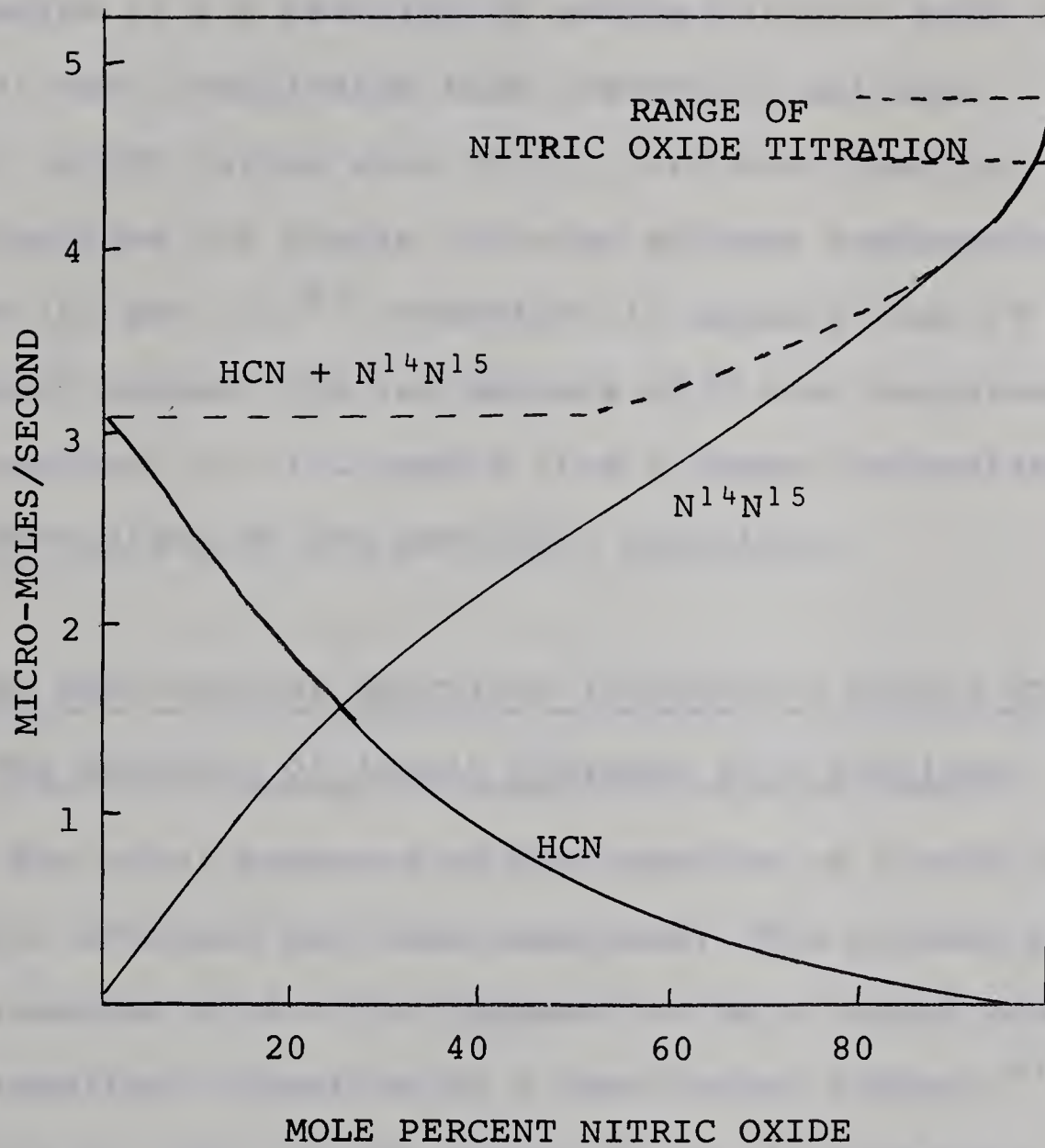
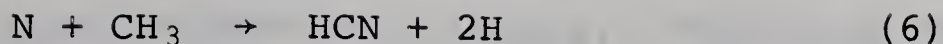


Figure 2

Results of Back and Fersht³⁸



followed by



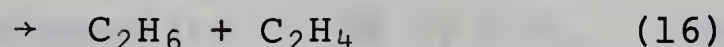
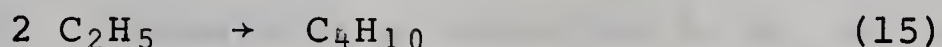
Also if NH_3 reacts with $\text{A}^3\Sigma_u^+ \text{N}_2$, then its addition upstream from NO should affect the NO titration. Such is not the case.³⁹ The results of Herron⁴⁰ clearly indicate that the mechanism of the reaction of active nitrogen with ethylene is far more complicated than previously believed. That the ratio $\Delta\text{N}/\text{HCN}$ varies with $[\text{C}_2\text{H}_4]_0$ and with reaction time clearly precludes the simple two-step process represented by reactions (5) and (6).⁴⁰ Therefore it appears that if the discrepancy between the two methods of N atom measurement is to be resolved, it will result from a deeper understanding of the mechanisms of the pertinent reactions.

SOME FREE RADICAL REACTIONS INVOLVING N AND/OR ETHYLENE.

A. The Reaction of Atomic Hydrogen with Ethylene

The major products of the reaction of H with C_2H_4 are ethane, n-butane and some acetylene. The primary process of the reaction of $\text{H} + \text{C}_2\text{H}_4$ appears to be a simple addition with the resultant formation of a "hot" ethyl radical.⁴¹ The ethyl radical is "hot" to the extent of ca. 40 kcal/mole of vibrational energy. Bradley and co-workers,⁴² in experiments on the photolysis of diethyl mercury, have shown that disproportionation becomes more important relative to recombination of ethyl radicals, if the C_2H_5 is "hot". It was estimated that these "hot" ethyl radicals survive ca. 10^5 collisions with neon before becoming thermalized. Cvetanovic⁴¹ notes

that this inefficiency of deactivation of "hot" C_2H_5 would seem unlikely for higher vibrational levels. Therefore the enhanced C_2H_6/C_4H_{10} ratio may not be entirely attributable to an enhanced disproportionation of ethyl radicals. The mechanism suggested by Cvetanovic was:



Turner and Cvetanovic⁴³ found a value for k_{-13} of $5 \times 10^8 \text{ sec}^{-1}$ while Rabinovitch⁴⁴ found $1.8 \times 10^7 \text{ sec}^{-1}$ in the corresponding $H + \text{trans ethylene } d_2$ reaction. The above mechanism predicted an increase in C_2H_6/C_4H_{10} with decreasing pressure, caused by an increase in the importance of reaction (17), rather than an enhanced disproportionation of ethyl radicals.

H atoms appear to react with ethylene with an activation energy of 5 kcal/mole and collision efficiency of ca. 10^{-3} .^{45,46}

B. The Reaction of Active Nitrogen and Atomic Hydrogen

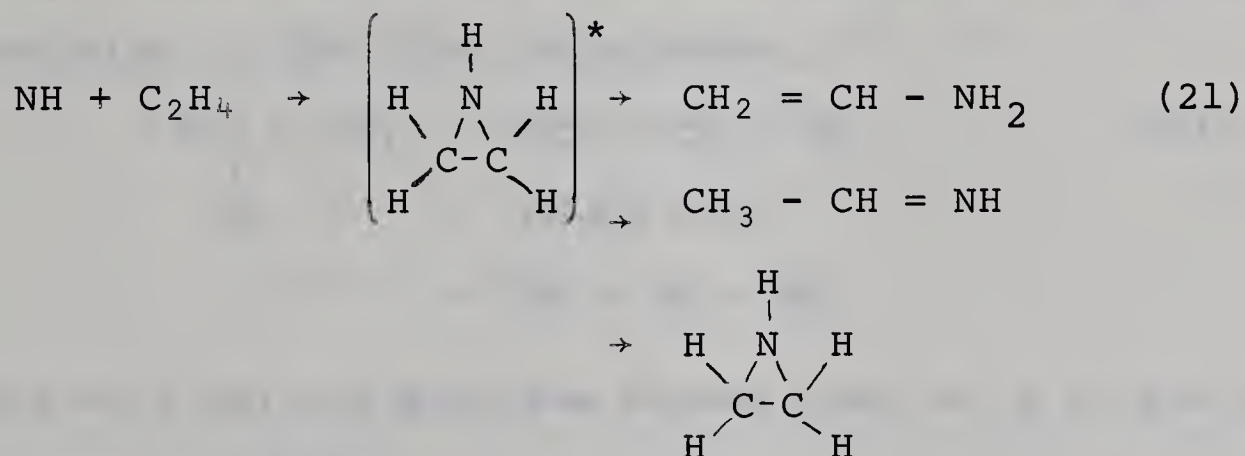
Although atomic nitrogen does not react with H_2 nor does atomic H with N_2 , when both atomic species are present, ammonia has been found to be produced.⁴⁷ Also NH has been observed in emission for the reaction $N + H$.^{48,49}

C. The Reaction of NH with C₂H₄

R.A. Back and co-workers^{50,51} have photolyzed isocyanic acid in order to produce imino radicals. They found that addition of C₂H₄ reduced the yield of CO, N₂, and H₂. They suggested that the residual CO resulted from



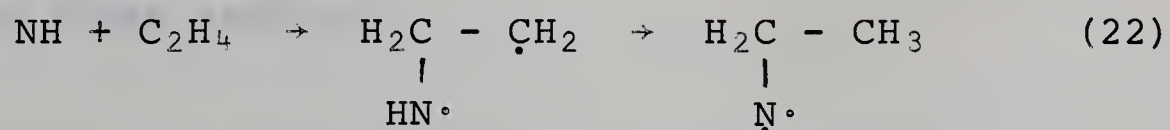
while the remainder resulted from secondary reaction of HNCO in the absence of C₂H₄. Therefore, a reduction in H₂, N₂ and CO yield is consistent with consumption of NH by C₂H₄. These authors suggest that NH adds across the double bond to form a "hot" ethylene imine molecule which then rearranges or is stabilized.



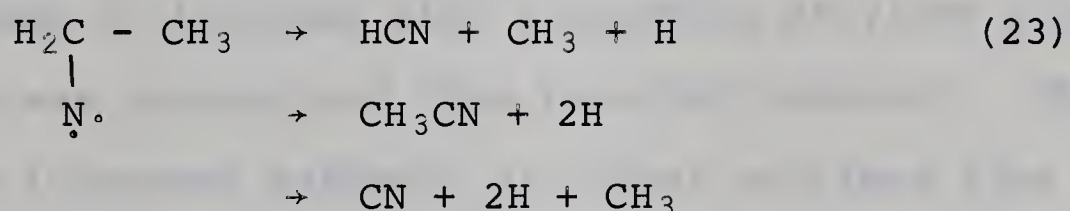
However, neither vinyl amine nor ethylene imine were found as stable products. Also they did not detect any HCN.

A more detailed investigation was carried out by Berry and co-workers.⁵² These authors studied the reaction of NH with olefins by the flash and isothermal photolysis of HN₃ in the presence of olefin. In the flash photolysis experiments the most prominent spectral features were the absorption of triplet NH in the ground state, NH(A³Π ← X³Σ⁻) and the violet bands of CN(B²Σ⁺ ← X²Σ⁺). No absorption was found

due to the short-lived $^1\Delta$ state of NH. In contrast to the results of Back, this work showed that HCN was a major product in both the flash and isothermal photolyses. Experiments involving the isothermal photolysis showed the products were HCN, CH_3CN , CH_4 , H_2 and an amorphous solid. These authors suggest an initial attack to the double bond of C_2H_4 , followed by a transfer of a hydrogen



The products are then formed by a split of any two bonds adjacent to C_α for the isothermal photolysis and all three bonds in the flash experiments. This accounts for the observation of CN absorption in the flash experiments.

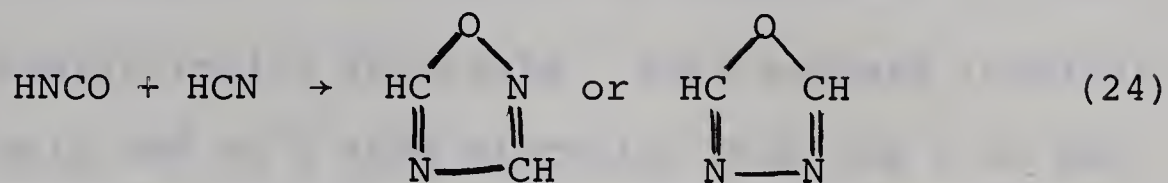


Experiments with DN_3 and ethylene showed that ca. $\frac{1}{2}$ of the D atoms appeared as CH_2DCN .

The postulate of the rearranged biradical intermediate was tested by photolyzing ethyl azide, $\text{CH}_3\text{CH}_2\text{N}_3$. CH_3CN , CH_4 , H_2 , and a gum were produced in the isothermal photolysis. The authors believe that HCN was also produced but was converted to gum. In the flash experiments the relative amounts of HCN and CH_3CN were about the same as that from $\text{C}_2\text{H}_4 + \text{HN}_3$ photolysis.

A possible explanation for the absence of HCN with Back's

experiments with HNCO is given by Berry and co-workers. HCN may be consumed by isocyanic acid, i.e.,



A rate constant of about 10^{-14} cc/molecule/sec for the disappearance of NH radicals in the presence of C_2H_4 has been estimated by these authors.

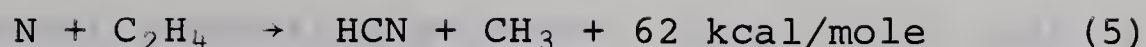
D. The Reaction of Active Nitrogen with Ethylene

The reaction of active nitrogen with ethylene was first studied by Greenblatt and Winkler.⁵³ They found the predominant product to be HCN and some ethane. The amount of HCN produced was found to increase with increasing ethylene flow until a maximum was reached and then remained constant. The yield of ethane increased markedly at higher ethylene flow rates.

Versteeg and Winkler⁵⁴ with improved experimental techniques were able to attain a carbon balance of about 96%. With ethylene in excess there was complete consumption of N atoms. At the flow rate in which both N and ethylene were completely consumed, the products of the reaction were HCN (75%), C_2H_6 (10%), CH_4 (9%), C_2H_2 (3%), and $(\text{CN})_2$ (2%). They also noted that the amount of $(\text{CN})_2$ increased rapidly with increased ethylene to a maximum but then decreased when ethylene was in excess.

Evans, Freeman and Winkler³³ assumed the primary reaction

step to be



since it is energetically favorable. This process involves a change in spin and an H atom migration from one C to the other. The CH_3 radical was then believed to react with another N via

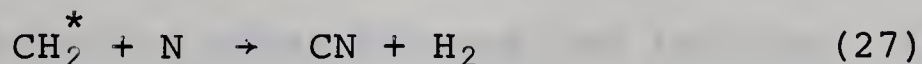
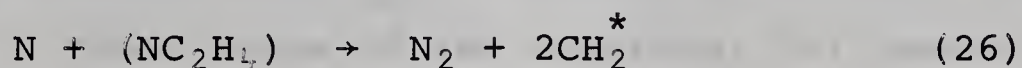


which is spin allowed for 3/8 of the collisions.

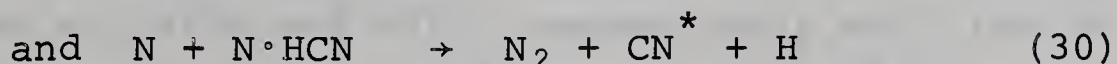
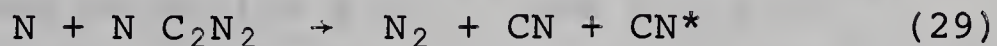
It was suggested that ethane was formed from the processes



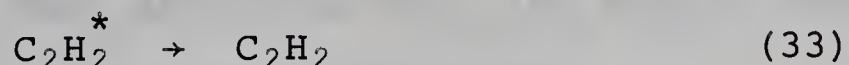
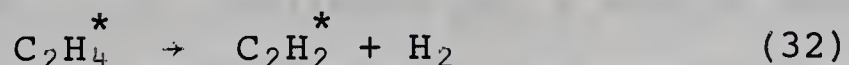
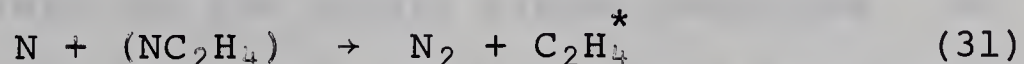
while $(\text{CN})_2$ was postulated to have arisen from the reaction between an N atom and a N-ethylene complex



The occurrence of the cyanogen flame in the N+ ethylene reaction was suggested to be due to

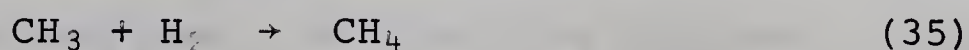


Acetylene formation presumably resulted from



These authors suggest that the occurrence of C_2H_2 and $(\text{CN})_2$ is therefore evidence for a catalyzed recombination of N atoms,

and state that the products CH_4 and C_2H_6 in the region of excess N represent supporting evidence. They reason that if the [N] were not markedly decreased in this region that reactions leading to $\text{CH}_4 + \text{C}_2\text{H}_6$ such as



could not compete with reaction (6).

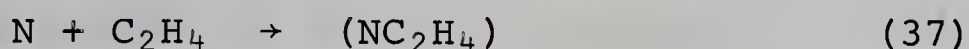
The kinetics of the reaction of N with ethylene were put on a more quantitative basis in a study by Levy and Winkler.⁵⁵ These workers attempted to study the reaction time as a parameter by investigating various methods of quenching the reaction. Among these methods were (a) cryogenic quenching, (b) addition of NO at a given stage of the reaction, (c) removal of an aliquot of the reacting gases through CuO turnings, (d) a CuO target technique, and (e) a cobalt target technique.

The techniques of NO addition and the cobalt probe yielded the most reliable results. The rate constant for N attack on ethylene was found to be 1.8×10^{-14} and 2.3×10^{-14} cc/molecule/sec at 295°K and 672°K respectively with the NO addition technique, and 1.7×10^{-14} and 3.0×10^{-14} cc/molecule/sec respectively for the cobalt target technique. An activation energy of (0.4 ± 0.2) kcal/mole and a steric factor of 10^{-5} was calculated. They attribute this low steric factor to the fact that reaction (5) is spin disallowed.

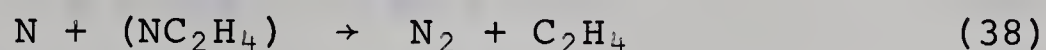
Other values for the same rate constant which have been

reported are 1.6×10^{-13} ,⁵⁶ 0.96×10^{-13} ,⁵⁷ and 0.17×10^{-13} cc/molecule/sec.⁴⁰ The last value however was calculated using a different mechanism.

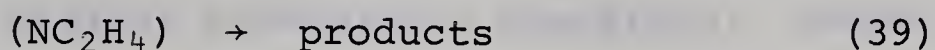
In a mass spectrometric study by Herron⁵⁷ it was discovered that most of the N atoms were destroyed without equivalent destruction of ethylene. He therefore proposed a mechanism compatible with this observation



followed by catalytic recombination



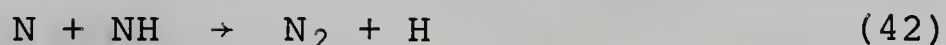
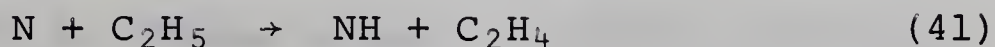
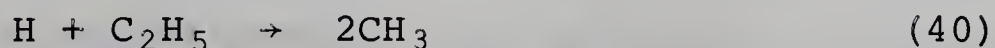
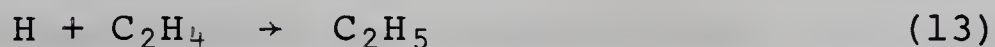
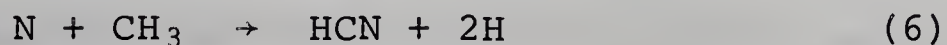
or by dissociation



This is identical with the mechanism of Evans, Freeman and Winkler.³³

In a later, more detailed study, Herron⁴⁰ found that H atoms play a major role in the reaction of N with C_2H_4 . Knowledge of several interesting features of the reaction resulted from this investigation. It was found that the ratio of N atoms destroyed to HCN molecules produced, $\Delta\text{N}/\text{HCN}$, was highest at low reaction times and low rates of ethylene input, and decreased to an apparently constant value at longer reaction times and higher ethylene input rates. Herron also found that this ratio was independent of the initial N atom concentration, in agreement with Verbeke and Winkler.³⁶ On this basis a catalytic recombination of N atoms, as previously proposed, was ruled out. Herron actually detected H atoms in his system

and at a sufficiently high concentration to play a major role in the reaction. He therefore mixed 2% H₂ with N₂ prior to activation in the discharge and noted a large increase in the HCN yield of the reaction. In view of these findings, Herron proposed the following mechanism to account for his results:



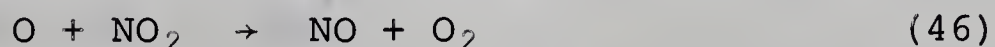
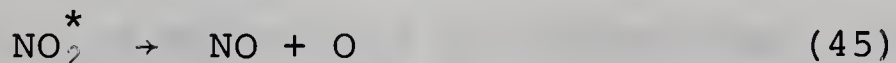
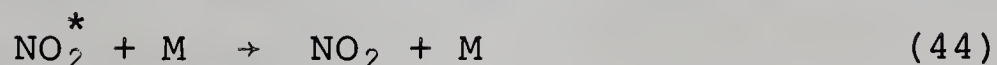
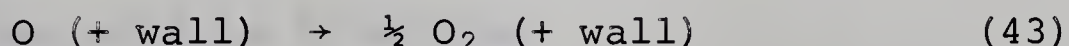
followed by atom and radical termination reactions. Herron points out that the most important feature of this mechanism is the competition between H atoms and N atoms for ethyl radicals in steps (40) and (41). This competition apparently determines whether the N atom will be detected as HCN or remain undetected as N₂. An increase in H atom concentration would favor reaction (40) relative to reaction (41) and therefore explain the observed decrease in ΔN/HCN ratio when hydrogen is added.

E. The Reaction of Active Nitrogen with Nitric Oxide.

The reaction of active nitrogen with NO was studied in some detail by Kistiakowsky and Volpi⁵⁸ using a mass spectrometer. They noted that, as NO was added in increasing amounts to active nitrogen, it was completely destroyed by N atoms.

At a certain rate of NO input, the N atoms were also completely destroyed. Above this rate no N were present and unreacted NO was measured. Below this critical flow rate, molecular O₂ began to form and increased to a plateau value with increased NO input.

Spectrograms of the radiation emitted from the reaction showed the usual afterglow and the β bands of nitric oxide when NO was present in comparatively low concentrations. At higher concentrations, this banded spectrum was masked by a continuum from ca. 6200 - 4200 Å. These authors found the following mechanism fitted their data:



The first two steps predominate at low rates of NO input. A rate constant of 7×10^{-13} cc/molecule/sec for the first step was determined. In subsequent work a value of $k_2 > 8 \times 10^{-11}$ was determined.³⁰ Clyne and Thrush⁵⁹ estimate $k_2 = 4.2 \times 10^{-11}$ cc/molecule/sec. None of the reaction steps above are exothermic enough to excite NO to the upper state of the β bands (129 kcal/mole). Excitation as the result of N atom recombination was then proposed.

Kaufman and Kelso⁶⁰ attempted to establish the source of excited NO when small amounts of NO were mixed with active

nitrogen. The coexistence of NO and active nitrogen was indeed puzzling since reaction (2) is very fast. The β NO emission was therefore postulated to result from



and the steady state concentration of NO would remain small. To establish this, they reacted active nitrogen with N^{15}O and noted that the resulting spectra were due to N^{14}O .

These authors therefore draw the following conclusions regarding the reaction of nitrogen with NO:

1. When small amounts of NO are added to active nitrogen, the Lewis-Rayleigh afterglow is diminished by reaction $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$ and some excited NO is produced via $\text{N} + \text{O} + \text{M} \rightarrow \text{NO}^* + \text{M}$ as long as N is in excess.

2. Addition of more NO consumes N until the NO bands disappear.

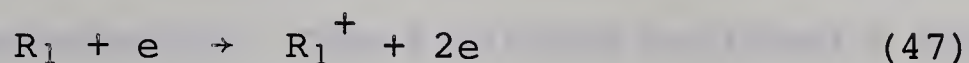
3. Further addition of NO results in a blue-green continuum resulting from $\text{O} + \text{NO} \rightarrow \text{NO}_2^*$.

In a later note, Kaufman and Kelso¹⁰ suggest that the N_2 produced from reaction (2) is vibrationally excited. Schiff and co-workers have estimated that the N_2 formed possesses ca. 24 kcal/mole of vibrational energy.³²

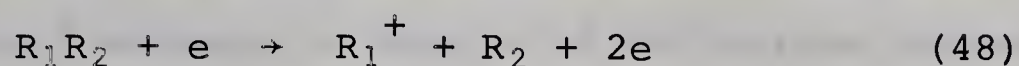
MASS SPECTROMETRY AND ITS APPLICATION TO ACTIVE NITROGEN

The detection of free radicals using mass spectrometry has been reviewed by Lossing^{61,62} and will only be treated briefly here. Also, the mass spectrometry of gases subjected to electrical discharge has been reviewed by Schiff.⁶³

In a normal mass spectrometer, which uses electron bombardment for ion production, radicals are detected as a result of the process



The radical ion however may also be produced via



Process (47) requires energy \geq ionization potential of R_1 to proceed while process (48) requires energy \geq the ionization potential of R_1 plus the dissociation energy of $R_1 - R_2$. The unequivocal detection of a free radical then depends on the difference in the energetics of these reactions. Ideally, the ion current can be made entirely due to the radical if the ionizing electron beam energy is greater than the ionization potential of the radical yet less than the appearance potential of the ion from the molecule R_1R_2 .

Radicals, however, sometimes evade detection for various reasons. The radicals may recombine before reaching the ion source either from wall collisions or collisions in the gas phase. Atoms in general are very sensitive to wall collisions, especially on metals while their recombination in the gas phase is relatively improbable. However, polyatomic radicals, which are often insensitive to wall collisions, generally recombine rapidly in the gas phase since a third body may not be required. On the other hand, the radicals may not be present in high enough concentrations to be detected. The fact that N_2 has a large dissociation energy (9.76 eV), and does not have a low lying excited state, coupled with the fact that N is not as

sensitive to wall collision as other atoms, makes N an almost ideal free radical for mass spectrometric investigation.

Jackson and Schiff^{8,9} were the first to study active nitrogen using mass spectrometry. These authors employed a condensed discharge and passed a stream of N₂ through the discharge. Downstream from the discharge, a sample of the stream passed through a leak sparked in a quartz thimble to the ion source of the mass spectrometer. The latter was a 90° sector instrument with 15.0 cm radius of curve. Back diffusion of gases was minimized by differentially pumping the filament chamber.

It was found that initiation of the discharge caused an increase in the ion current at $m/e = 14$. A study of the dependence of the ion current at $m/e = 14$ on electron beam energy (ionization efficiency curve) showed a species having an ionization potential of 14.7 ± 0.2 eV and another species with an appearance potential of 16.1 eV. The spectroscopic ionization potential for (¹⁴S)N is 14.54 eV. Thus, the presence of (¹⁴S)N in active nitrogen was established. The nature of the second species present however, could not be established.

Soon after the work of Jackson and Schiff, a mass spectrometric study of the nitrogen afterglow was made by Kistiakowsky and co-workers.⁶⁴ The instrument employed had a 60° analyzer and a 12 inch radius of curvature. The molecular leak was made by sparking a Tesla coil through a mica sheet of 25 μ thickness. The ionization chamber was a Faraday cage. No electron trap or ion repeller was used but the ionization chamber did have a regulator circuit for both electron

emission and beam voltage. They found no discontinuity in the ionization efficiency curve for $m/e = 14$ of the type found by Jackson and Schiff. Examination of the curves for $m/e = 28$ showed some ion current at low electron beam energies with the discharge on. This was interpreted as evidence for a metastable molecular species in active nitrogen. However, when the geometry of the system was made more favorable, no increase in this peak magnitude was observed. They therefore rationalized the early onset of ion current in terms of impurity fragments decomposed in the discharge. The afterglow intensity was found to vary as the square of the ion current at $m/e = 14$, which was consistent with the afterglow resulting from the recombination of 2 N atoms. Added argon and helium were found to increase the intensity at constant total pressure and atom concentration whereas oxygen had no effect.

That metastable atomic and molecular species were not detected by these workers is not surprising, since wall deactivation would undoubtedly be very efficient. Foner and Hudson⁶⁵ have employed a molecular beam sampling system. Species therefore traversed a collision free path to the ion source. Species were ionized by electron impact and, after mass separation by a 90° magnetic sector analyzer, were post-accelerated by a few thousand volts to an electron multiplier. When nitrogen, with a large excess of added helium, was subjected to electrical discharge, excited N atoms were detected, namely the 2D and 2P states. The relative concentration of N atoms in the 4S , 2D , and 2P states were estimated to be in the

ratio 1.00 to 0.17 to 0.06. The excited atoms were only observed within ca. 1 msec after leaving the discharge. Using a high power discharge excited N atoms were found in pure discharged nitrogen but were only about 1/25 as abundant as they were with helium present. Metastable molecular N_2 , believed to be vibrationally excited N_2 in its $X^1\Sigma_g^+$ state and electronically excited $A^3\Sigma_u^+ N_2$ were also found to be present.

THE PRESENT WORK

Studies of the reaction of active nitrogen with ethylene have proceeded to the point where the reaction is now known to be far more complex than originally envisaged. An understanding of the ethylene reaction is of two-fold importance. Since ethylene is the simplest of the olefins, it is the logical molecule to investigate in order to understand the interaction of N with olefins in general. Also, since the maximal HCN yield from this reaction has been used as a measure of the N atom content in the system, in disagreement with the NO titration method, an attempt should be made to explain mechanistic features in terms of this discrepancy, and vice versa. To this end, the present work has been directed.

EXPERIMENTAL

MATERIALS

Nitrogen (Linde prepurified and Canadian Liquid Air) was passed through a 'U' trap filled with glass helices. In most experiments the trap was maintained at -195° . Nitric oxide (Matheson) was purified by repeated distillation through 'U' traps at -160° . Reagent grade C_2D_4 and C_2D_3H (Merck, Sharpe and Dohme of Canada) were degassed prior to use. C_2H_4 was purified by repeated distillation through 'U' traps at -130° .

THE VACUUM SYSTEM

The vacuum system used in the present work is shown in Fig.3 and consisted of four main sections: the nitrogen flow system (and also in later experiments, a hydrogen flow system), the reactant flow system, the reaction chamber and the analysis system. The nitrogen flow system consisted of a 'U' trap, a mercury manometer and a calibrated ballast volume. The reactant flow system consisted of two 2-liter bulbs and a mercury manometer. The nitrogen and reactant sections were connected to the reaction chamber through two fine control needle valves (Edwards High Vacuum Corp.). An enlarged view of the reaction chamber is shown in Fig.4. The reaction chamber was 18 mm of Pyrex tubing 40 cm in length. Coaxial with the chamber was a movable reactant inlet. The inlet was connected to the reactant system by two 'O' ring connections which enabled movement of the inlet along the chamber while operating under vacuum. Downstream from the reactant inlet, a leak into an MS 10 mass

Figure 3

The Vacuum Apparatus

- A 'U' trap filled with glass helices
- B Calibrated Ballast Volume
- C Fine Control Needle Valves
- D Reactant Gas Storage Bulbs
- E Resonance Cavity
- F 'O' Ring Connections
- G Reaction Tube
- H Movable Reactant Inlet
- I Leak to Mass Spectrometer

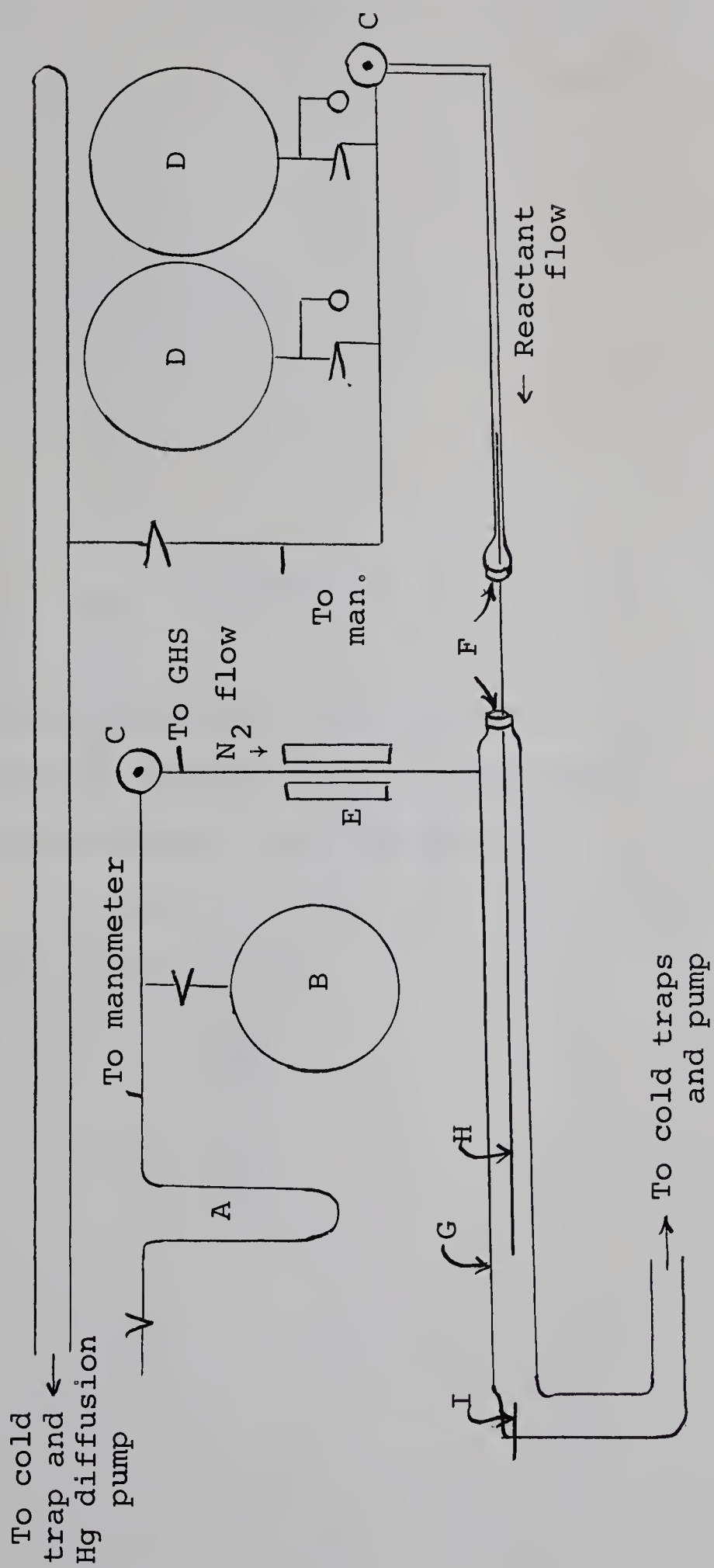
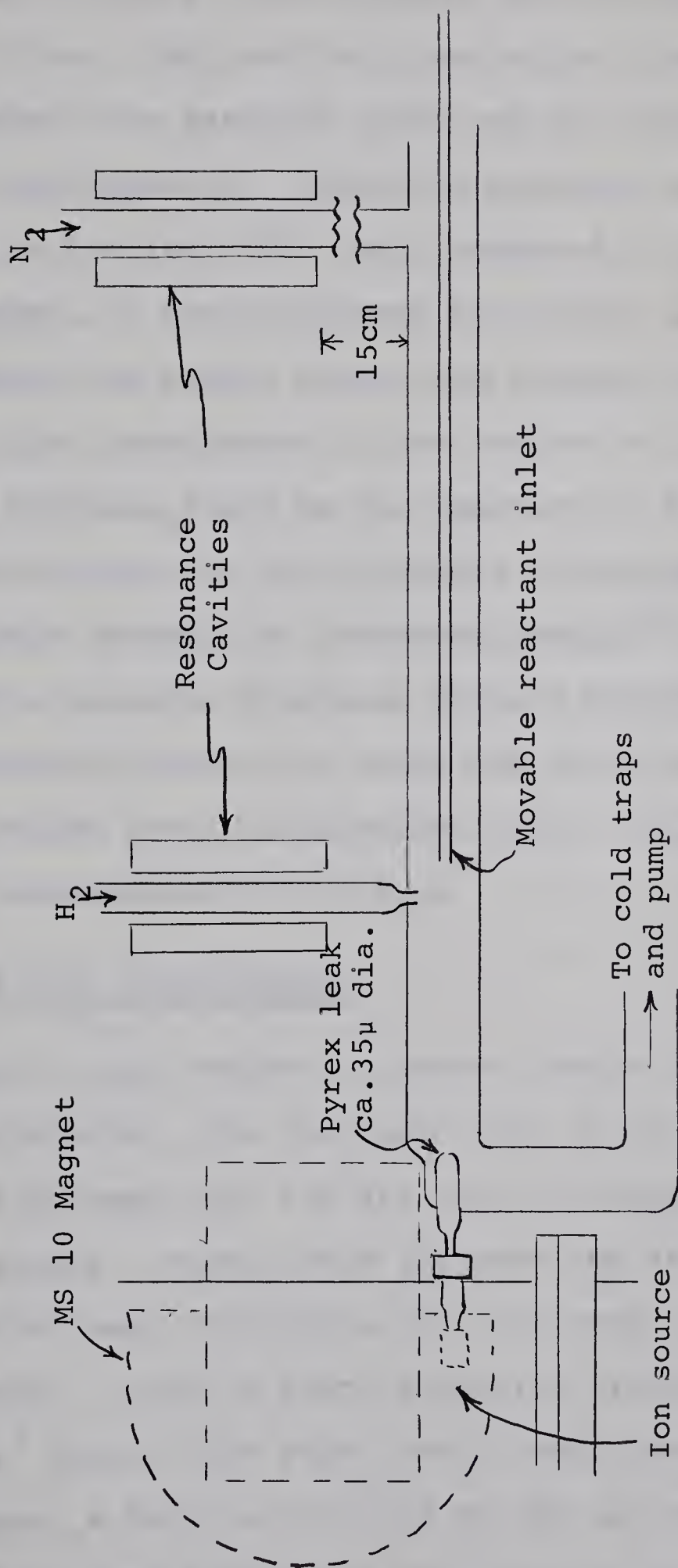


Figure 4

Enlarged View of Reaction Tube
(also showing modification for hydrogen
atom addition experiments)



spectrometer (Associated Electrical Industries) was located, also shown in Fig.4. The movable inlet was used to vary the reaction time. The reaction time varies directly as the distance between the reactant inlet and the molecular leak into the mass spectrometer. Since the pressure in the mass spectrometer is low (ca. 10^{-5} torr) compared to that in the reaction chamber, it can be assumed that there is no further reaction after the sample gases pass through the leak.

In later experiments it was desired to study the effect of added hydrogen atoms on the reaction of N and ethylene. Rather than premixing the molecular nitrogen and hydrogen before passage through the resonance cavity,⁴⁰ it was decided to employ a separate discharge for the hydrogen, and allow the discharged hydrogen to enter the reaction chamber at a fixed distance from the molecular leak. This modification is shown schematically in Fig.4.

THE MS 10 MASS SPECTROMETER

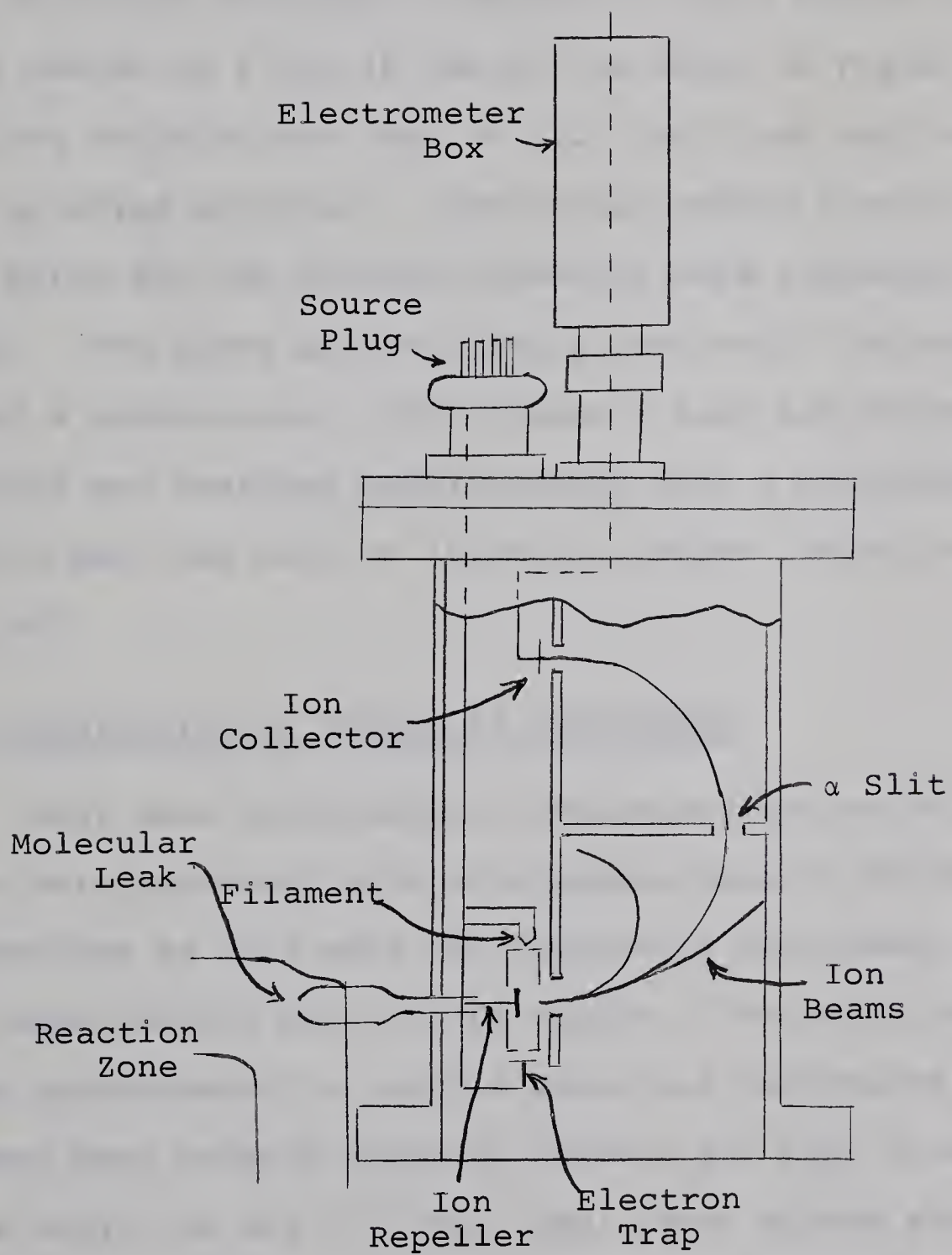
Since it was desired to detect atomic nitrogen with the mass spectrometer, the instrument had to be modified. The factory instrument had the gas inlet located ca. 10 cm from the ion source. Within this distance the atomic nitrogen would suffer many collisions with the metal interior of the spectrometer. Since N atoms recombine efficiently on metal surfaces,⁵ none of the atoms would reach the ion source. For this reason, a hole was drilled to the ion source. Through this, a 5 cm long Pyrex lead ran from the ion source to the

molecular leak and was held in place with an 'O' ring connection. This lead could not be made shorter because of the design of the spectrometer. The ion source of the MS 10, which is normally of quite open construction, was closed off by the insertion of metal strips which formed the walls of an ion box. This was done since the pumping speed near the ion source is only moderate (approximately 15 l/sec). The closed construction increased the probability that only freshly arriving sample entered the ion source.

The source and collector units of the MS 10 are shown in Fig.5. The MS 10 is a 180° deflection instrument with a 5.08 cm radius of curvature. Its ion source consists of a filament of 0.5 ohm rhenium wire which yields a bombarding electron beam of 5 to 105 eV energy. The intensity of the electron beam can be set at 10 μ A or 50 μ A trap current. Expulsion of the positive ions out of the source through the resolving slit is aided by an ion repeller which can be varied from -5 to 10 volts with respect to the cage. The ions are accelerated into the analyzer region by a variable cage potential of 40 to 2000 volts d.c. with respect to ground, depending on the mass of the ion being resolved. In the analyzer region the ions are resolved with an 1830 gauss magnetic field, and finally pass through a 0.051 mm collector slit to the collector. The collector is an electrometer box type ME1403 (AEI) with an input resistance of 10^{11} ohms. The mass spectrometer was evacuated with a Duo Seal mechanical forepump (W.M. Welch Manufacturing Co.) and a Metrovac High Vacuum oil diffusion pump (AEI).

Figure 5

Source and Collector Units of the MS 10 Instrument



With its cold trap filled with liquid nitrogen, the tube unit could be evacuated to less than 10^{-7} torr in the absence of gases entering from the reaction system.

Molecular leaks for the mass spectrometer were made by the following technique: lengths of Pyrex having shoulders were sealed to a tip at one end as shown in Fig.6A. An electrolyte solution was used to fill the Pyrex and to mix with the grinding material. Electrodes leading from the inside of the Pyrex and the grinding material were connected to an ohmmeter. The Pyrex tip was then ground until the meter registered a conductance, which showed a leak had formed. The leak diameter was measured approximately with a microscope and then a ring seal was made to 18 mm i.d. Pyrex tubing as shown in Fig.6B.

THE SENSITIVITY OF THE MS 10 INSTRUMENT

Most mass spectrometric determinations on this instrument were conducted with an electron beam of 20 eV energy. Exceptions to this were the ionization efficiency curves and the measurements made of HCN yields. The sensitivity of the mass spectrometer to various gases was determined from the parent peak heights observed (except for C_2H_4 in which the peak height at $m/e = 26$ was used) after mixing known amounts of the gases with the correct amount of nitrogen. A gas handling system, shown in Fig.7, facilitated sensitivity measurements.

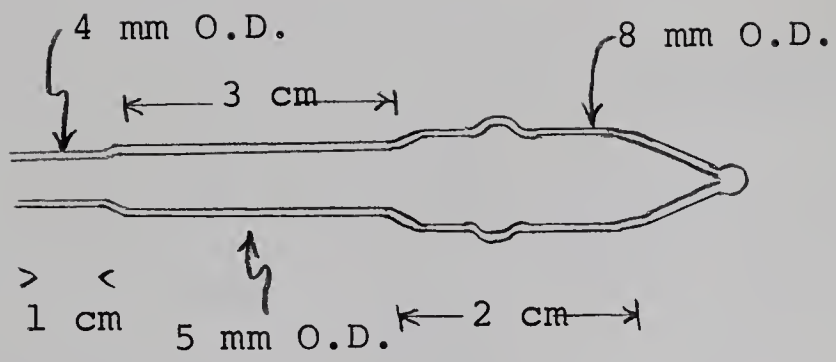
Typically, a sensitivity measurement was conducted in the

Figure 6

Molecular Leak Assembly

- A Before Grinding
- B After Grinding and Ring-Sealing
to Reaction Tube

A



B

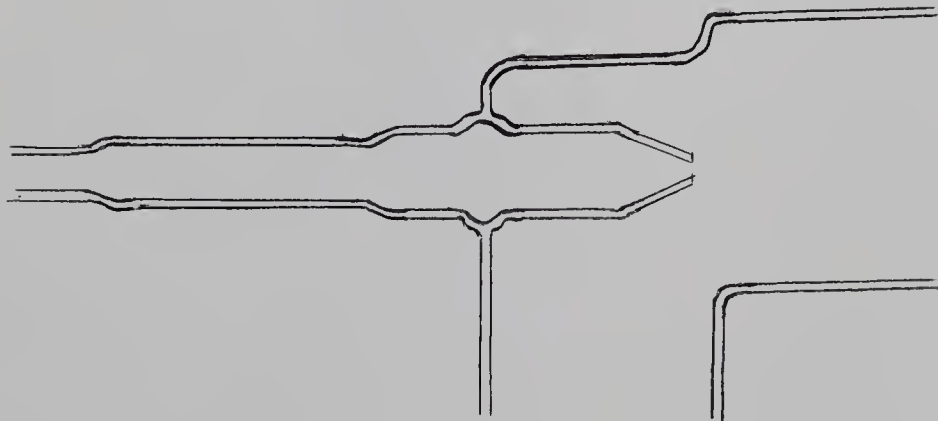
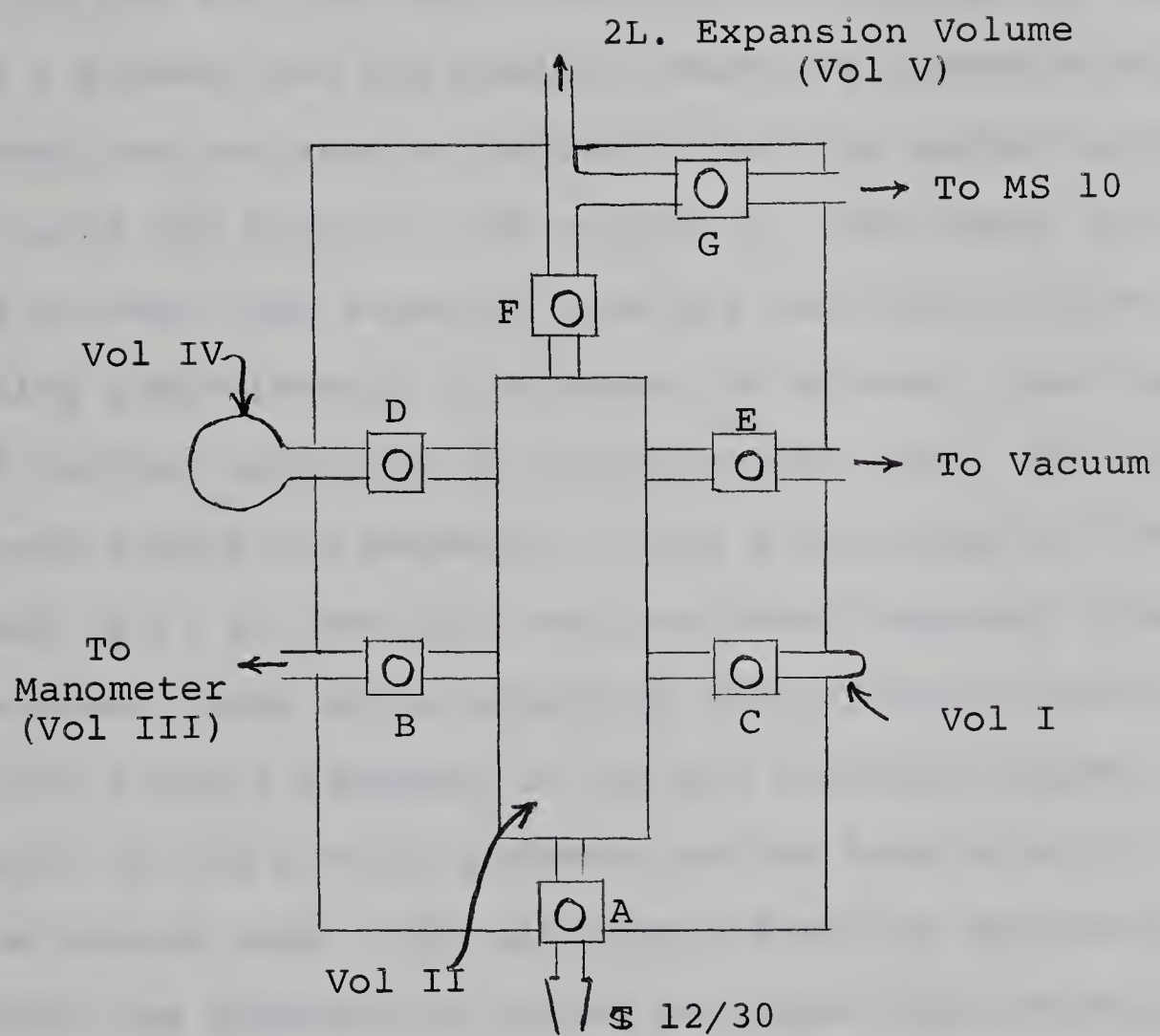


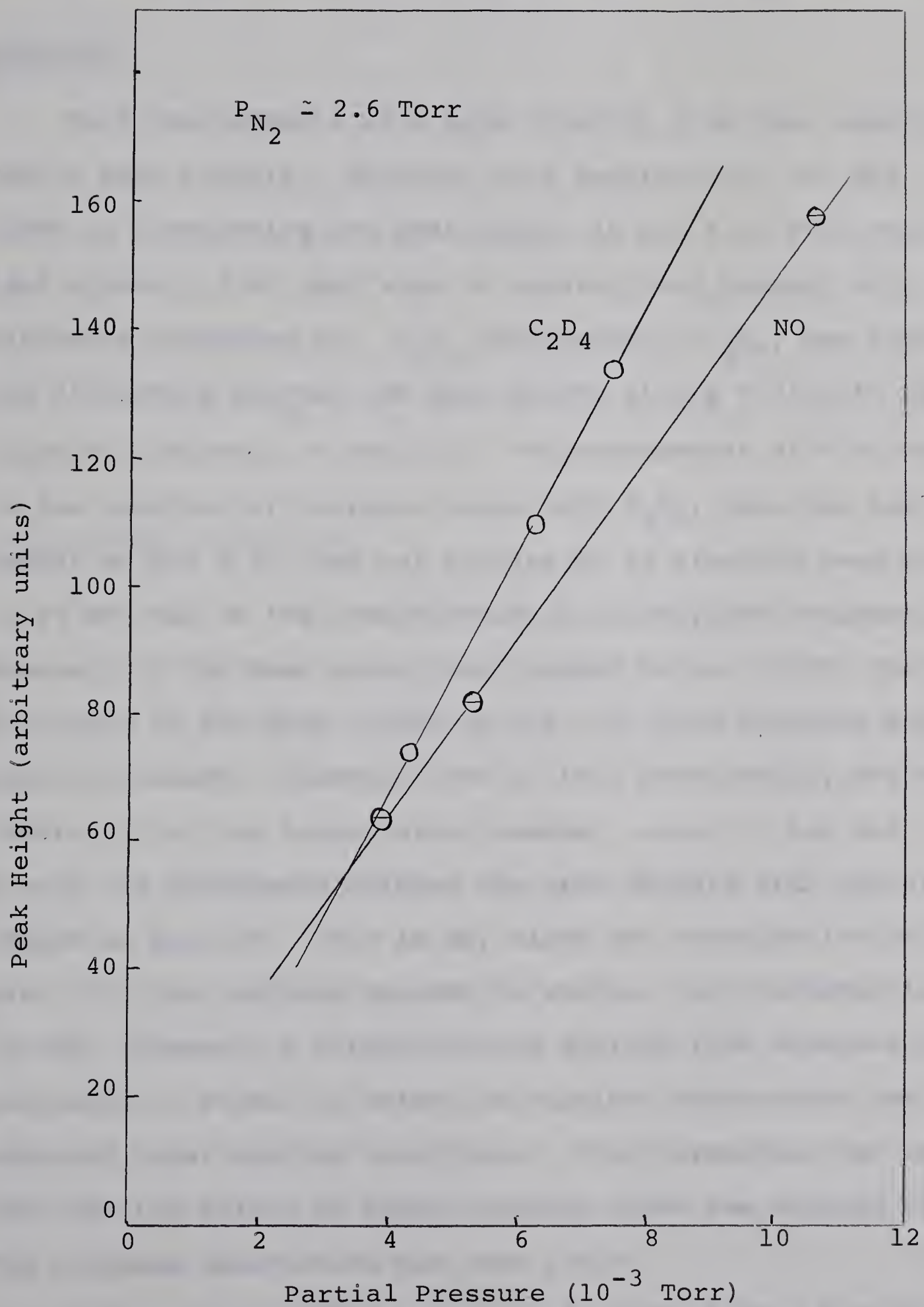
Figure 7
Gas Handling System



following manner: first, some of the gas in question was admitted to the gas handling system through valve A, as shown in Fig.7. Its pressure was then measured with the mercury manometer and the valve C was then closed. After evacuation of the remainder of the system, the gas in this volume I was expanded to volumes II and III. The small volume I was again isolated and the remainder evacuated. Nitrogen was then added as a diluent and its pressure measured approximately. The nitrogen was isolated in volume IV and the system again evacuated (with the exception of volume I). The gases in volumes I and IV were then expanded into the two liter volume V. After allowing approximately 15 minutes for mixing, there was a small further expansion to the molecular leak. The appropriate peak height was measured. From a knowledge of the precise volumes of I, II, and III, and the total expanded volume of the system, there is an expansion factor which, when coupled with the initial pressure in the gas handling system, leads directly to the partial pressure on the high pressure side of the molecular leak. The nitrogen diluent is necessary to simulate the composition during an actual flow experiment, since the sensitivity of the diluted gas is lower than the sensitivity of the pure gas. Sensitivities were measured periodically for each gas since they did change somewhat. Typical of the sensitivities determined are those shown in Fig.8. The sensitivity of the instrument to nitrogen atoms was determined by means of the reaction of nitrogen atoms with nitric oxide.⁵⁸ From the amount of NO destroyed, with

Figure 8

Typical Sensitivity Plots for C_2D_4 and NO



NO in slight excess, and the sensitivity of the mass spectrometer to NO, the sensitivity to N atoms could be determined.

ANALYSIS

Most measurements were made directly from mass spectrometric peak heights. Nitrogen atom destruction, ΔN , was found by subtracting the peak height at $m/e = 14$ with reactant present, from that when no reactant was present with the microwave discharge on. C_2D_4 destruction, ΔC_2D_4 , was simply the difference between the peak height at $m/e = 32$ with the nitrogen discharge on and off. The measurement of HCN formed in the reaction of nitrogen atoms with C_2H_4 , from the peak height at $m/e = 27$, was not precise at an electron beam energy of 20 eV, due to the interference of an ethylene fragment peak. However, if the beam energy was lowered to ca. 10 eV, the contribution to the peak height at $m/e = 27$ from ethylene was greatly reduced. However, even at this beam energy, the HCN determination was complicated somewhat, since it was not simply the difference between the peak heights with the discharge on and off. This is so, since the contribution to $m/e = 27$ from ethylene depends on whether the discharge is on or off. However, a correction was applied from separate experiments in which the extent of ethylene destruction was measured under similar conditions. This correction was largest when the effect of added hydrogen atoms was studied since the ethylene destruction was very large.

In some cases, HCN was measured by the Liebig titration

method⁶⁶ in the following manner: the products of the reaction of N with ethylene were removed from the nitrogen stream by a trap at -196° . After a certain time interval the nitrogen discharge, the ethylene flow and the molecular nitrogen flow were arrested and the system evacuated. Excess ethylene was removed by pumping on the trap raised to -130° . The contents of the trap were then transferred to another trap containing 1 N NaOH ice at -196° . This trap was removed from the vacuum line and warmed to room temperature. The resulting solution of NaCN was then titrated with standard AgNO_3 solution.

EXPERIMENTAL PROCEDURE

Experiments were performed at 0.6 and 2.6 torr of nitrogen. Flow rates of the nitrogen in the reaction tube were 34.5 and 225 $\mu\text{moles/sec}$ respectively, which gave average linear velocities of 422 and 666 cm/sec at the two different pressures.

For a typical experiment, the nitrogen was partially dissociated in a fast flow system by passage through a microwave resonance cavity (Ophthos Instrument Co.) coupled with an Hg 198 microwave exciter (Baird Atomic Co.) of 2450 Mc/sec output. When a constant ion current at $m/e = 14$ was obtained, reactant was added through the fine control needle valve behind the movable reactant inlet. A constant reactant flow rate was maintained by keeping the liquified reactant at some low temperature such that it had a constant vapor pressure of

ca. 100 - 200 torr behind the Edwards valve.

Relative afterglow intensity measurements were made with a portable photosensitive search head (Photovolt Corp.). The correlation between peak height at $m/e = 14$ and afterglow intensity was tested by strapping the photosensitive search head to the reaction tube, near the leak to the mass spectrometer. The search head, placed upstream from the ethylene inlet was also used to obtain initial nitrogen atom concentrations in some experiments where the ratio of N atoms destroyed/ethylene molecules destroyed was studied as a function of initial N atom concentration.

A comparison was made between a poisoned and an unpoisoned system for the reaction of N and ethylene. The most common technique of poisoning, that of coating the walls of the reaction chamber with metaphosphoric acid would have been difficult experimentally because of the presence of the molecular leak to the mass spectrometer. It was therefore decided to poison the walls with water vapor. If the nitrogen was bubbled through water at room temperature or even at 0°C however, too much water was present and the resultant nitrogen atom concentration was lower, rather than higher, than the nitrogen atom concentration in the unpoisoned system. Another very simple procedure, however, worked well. Most of the results were obtained using nitrogen which was passed through glass helices at -196° . Some of the results were obtained with the glass helices maintained at room temperature, so that traces of water vapor were admitted into the vacuum system.

These experiments can be described as occurring in a "poisoned" system whereas, when the liquid nitrogen was placed on the nitrogen line, the experiments can be described as occurring in an "unpoisoned" system. For experiments in the "poisoned" system, the nitrogen atom concentration was ca. 60% higher than it was when the system was "unpoisoned", for the same power output on the microwave exciter.

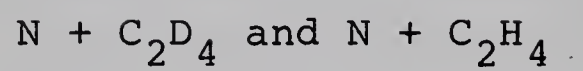
RESULTS

The reaction of active nitrogen with ethylene is characterized by a pink reaction flame extending downstream from the point of ethylene injection. At low ethylene input rates the flame extends all of the way down the tube and is superimposed upon the nitrogen Lewis-Rayleigh afterglow. As the rate of ethylene input is increased the flame decreases in length but increases in intensity while the Lewis-Rayleigh afterglow decreases in intensity. At high input rates, the flame is only a few cm long and the afterglow is completely extinguished downstream.

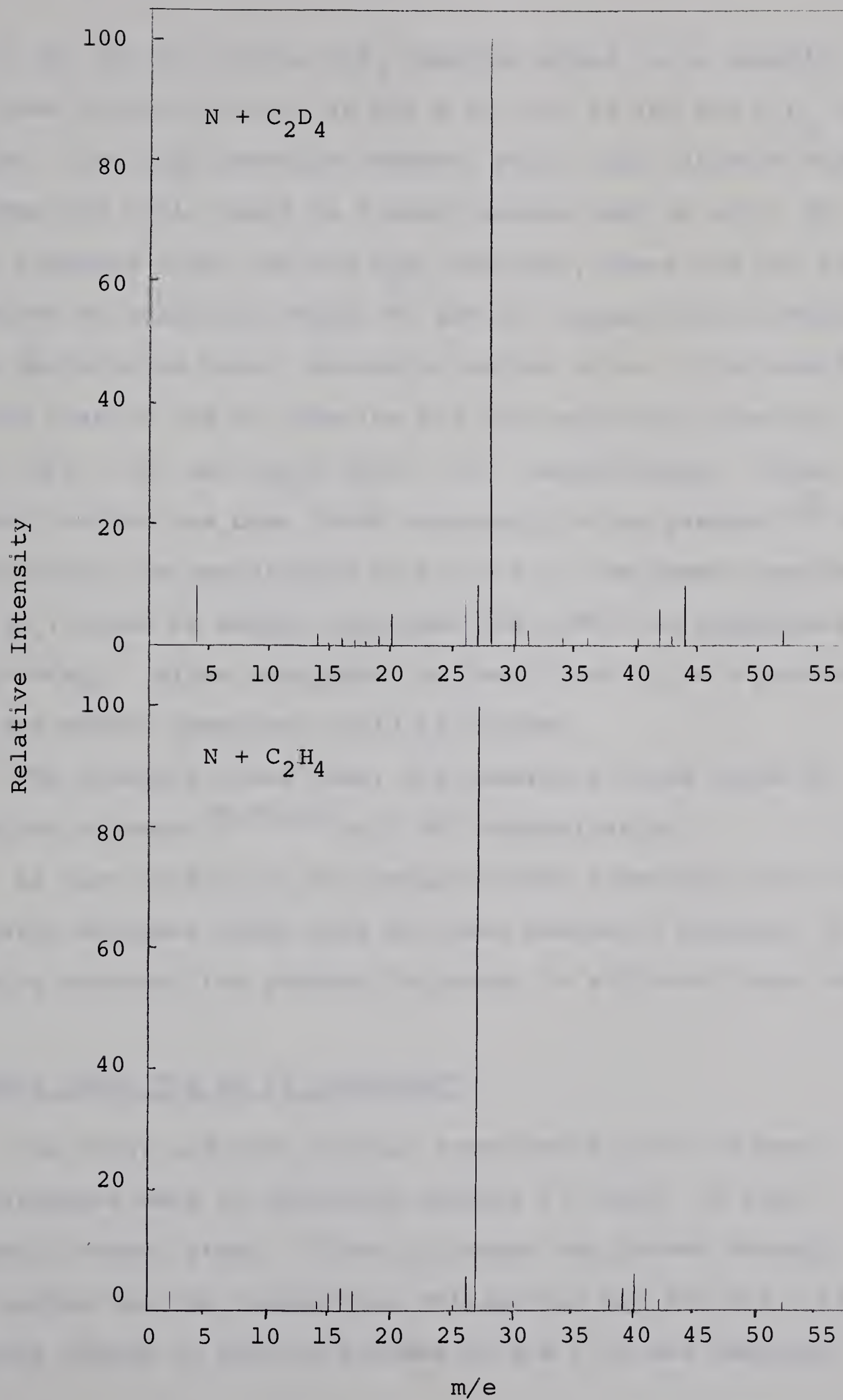
Fig.9 shows mass spectra of the products of the reaction of active nitrogen with C_2H_4 and C_2D_4 . These spectra were obtained after doing control experiments with C_2H_4 and C_2D_4 in N_2 with discharge off. Odd numbered masses, which are observed in the $N + C_2D_4$ mass spectrum are undoubtedly due to some C_2D_3H impurity in the C_2D_4 . HCN ($m/e = 27$) is the major product of the $N + C_2H_4$ reaction. Peaks from $m/e = 14$ to 17 show that traces of CH_4 and NH_3 are also formed, which have parent peaks at $m/e = 20$ for the C_2D_4 reaction. Since DCN and N_2 have a molecular weight of 28 in common, the ion current due to DCN at $m/e = 28$ was calculated approximately from the magnitude of the $m/e = 27$ peak height for the C_2D_4 reaction. The region from $m/e = 38$ to 44 for both the C_2H_4 and C_2D_4 reactions is of interest. For the C_2D_4 reaction, the peak at $m/e = 44$ is the most intense in this region. If methyl cyanide were the sole contributor, then the peaks at

Figure 9

Mass Spectra of the Products of the Reactions



(for original data see Table I in Appendix)



$m/e = 39, 40, 41$ for the C_2H_4 reaction would be in roughly the same intensity ratio as $m/e = 40, 42, 44$ for the C_2D_4 reaction. The C_2H_4 spectrum however, shows that although there is some $m/e = 41$, there is a more intense peak at $m/e = 40$. This suggests that, for the C_2H_4 reaction, there are two minor products of molecular weight 40 and 41, respectively, which, upon deuteration have a molecular weight of 44. This would be the case if the two species had the empirical formulae C_3H_4 ($m/e = 40$) and C_2H_3N ($m/e = 41$), respectively. Since methyl cyanide has been found previously to be present,⁴⁰ it is probably the contributor to $m/e = 41$. The former species, if C_3H_4 , could be methyl acetylene ($CH_3-C\equiv CH$) or propadiene ($CH_2=C=CH_2$). Since acetylene has been found to be a product,⁵⁴ perhaps methyl acetylene would be favored.

The products found then, are generally those found by previous workers,^{53,54,40} with HCN predominating.

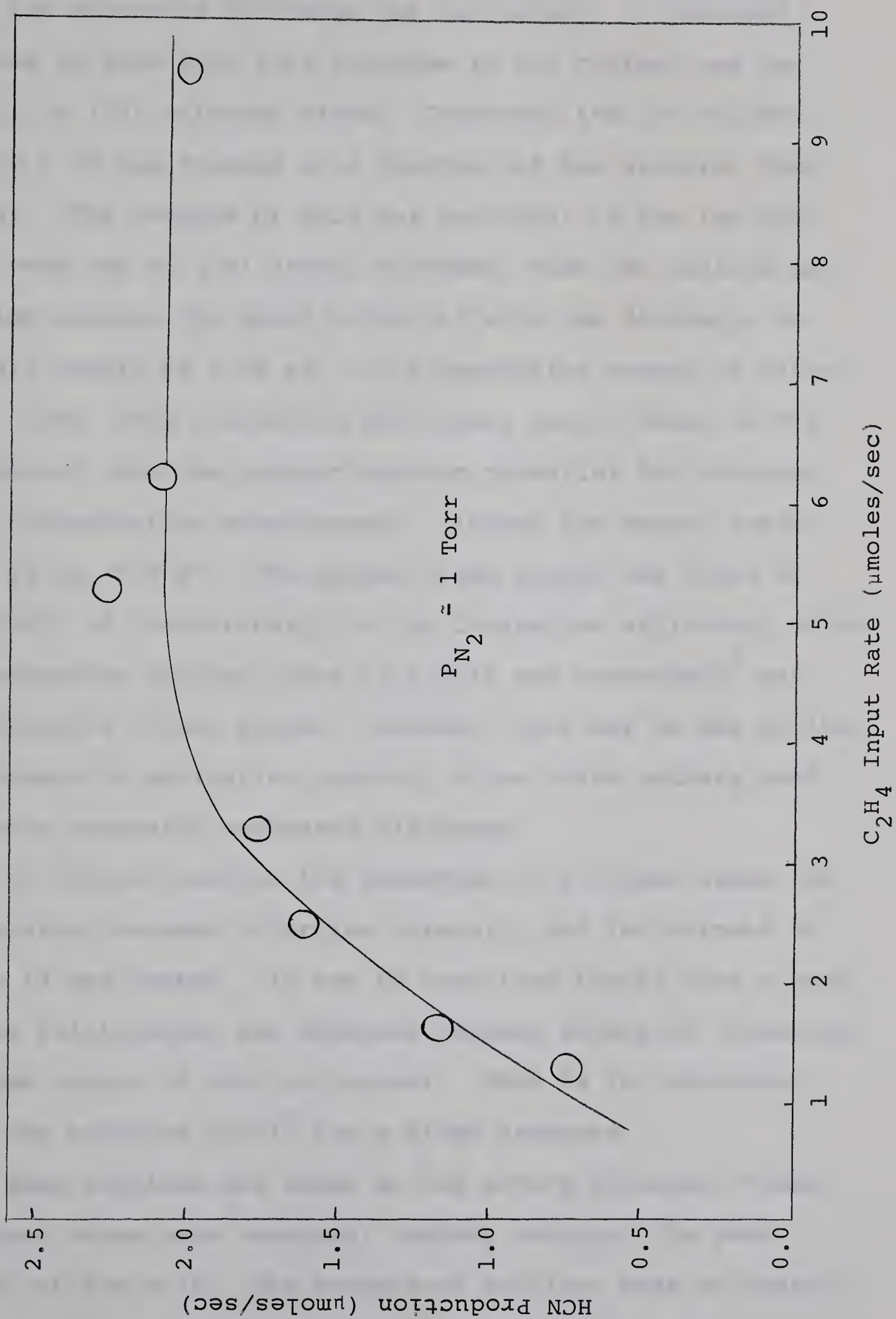
As seen in Fig.10, the amount of HCN increases with increasing ethylene input rate and then reaches a plateau, remaining constant for further increases in ethylene input rate.

RESULTS USING THE MS 10 INSTRUMENT

The first and most crucial experiments with the mass spectrometer were to determine whether it would, in fact, detect nitrogen atoms. First, nitrogen was passed through the system and the accelerator voltage was set for $m/e = 14$. A large change in the ion current at $m/e = 14$ was observed

Figure 10

HCN Production from the Reaction $\text{N} + \text{C}_2\text{H}_4$
as a Function of
Initial Ethylene Input Rate
(cf. Table 2 in Appendix)



when the microwave discharge was initiated. It remained however to show that this increase in ion current was due solely to (^4S) nitrogen atoms. Therefore the ion current at $m/e = 14$ was studied as a function of the electron beam energy. The purpose of this was two-fold: if the ion current were due to (^4S) atomic nitrogen, then the voltage separation between the onset potential with the discharge on and off should be 9.76 eV, the dissociation energy of nitrogen. Also, this ionization efficiency curve, shown in Fig. 11, should show the optimum working potential for nitrogen atom concentration measurements. Indeed the energy separation is ca. 9.8 eV. The optimum beam energy was found to be 20 eV. A discontinuity in the ionization efficiency curve, corresponding to that found by Schiff and co-workers⁹ was not observed in our system. However, this may be due to the difference in excitation sources, since these authors used the more energetic condensed discharge.

To further confirm the detection of nitrogen atoms the correlation between afterglow intensity and ion current at $m/e = 14$ was tested. It can be seen from Fig. 12 that a good linear relationship was obtained between afterglow intensity and the square of the ion current. This is in accordance with the relation $I \propto [\text{N}]^2$ for a given pressure.

When ethylene was added to the active nitrogen stream, nitrogen atoms were consumed, thereby reducing the peak height at $m/e = 14$. The deuterated ethylene made no contribution to the ion current at $m/e = 14$ and so its use

Figure 11

Semilogarithmic Ionization Efficiency Curves

for $m/e = 14$

(cf. Table 3 in Appendix)

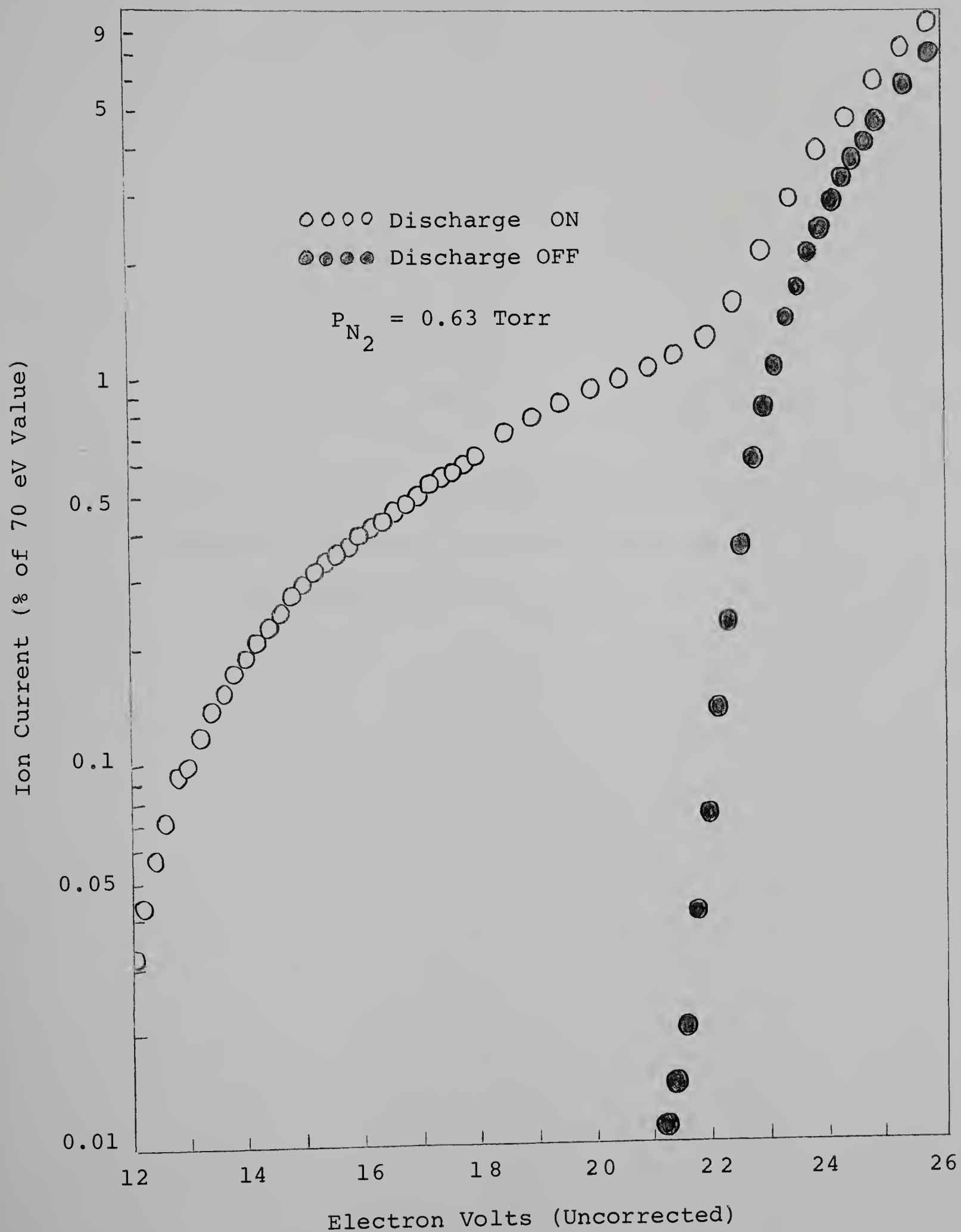
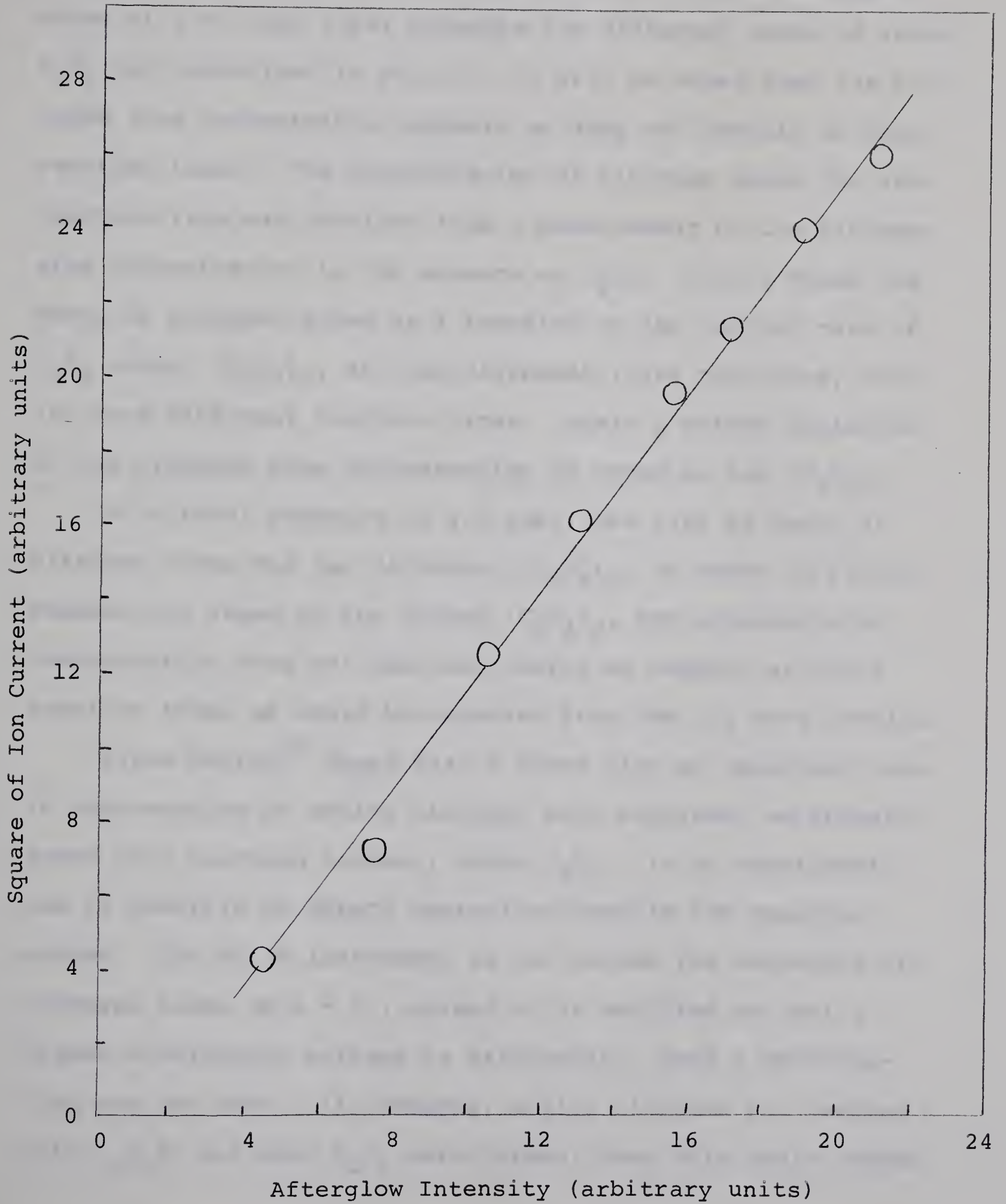


Figure 12

Dependence of the Square of the Ion Current
at $m/e = 14$ on the Afterglow Intensity
(cf. Table 4 in Appendix)



facilitated precise measurements of the decay of atomic nitrogen in the reaction zone. The rates of decay of nitrogen atoms at 0.63 torr total pressure for different rates of input C_2D_4 are summarized in Fig.13. It will be noted that the nitrogen atom concentration appears to drop off rapidly at short reaction times. The concentration of nitrogen atoms for zero reaction time was obtained from a measurement of the nitrogen atom concentration in the absence of C_2D_4 . Fig.14 shows the decay of nitrogen atoms as a function of the initial rate of C_2D_4 input, $(C_2D_4)_0$, at four different inlet positions, that is, four different reaction times. Again a marked depletion of the nitrogen atom concentration is noted at low $(C_2D_4)_0$.

At a total pressure of 2.6 torr, the rate of decay of nitrogen atoms for two different $(C_2D_4)_0$, is shown in Fig.15. However, as shown at the higher $(C_2D_4)_0$, the nitrogen atom concentration does not decrease nearly as rapidly at short reaction times as would be expected from the 0.6 torr results.

Since Herron⁴⁰ found that H atoms play an important role in the reaction of active nitrogen with ethylene, we investigated this reaction further, using C_2D_4 . In no experiments was it possible to detect deuterium atoms in the reaction system. The MS 10 instrument is not suited for detection of hydrogen atoms ($m/e = 1$), unless it is modified so that a higher accelerator voltage is attainable. Such a modification was not made. If, however, active nitrogen was reacted with C_2D_3H , and some C_2D_4 were formed, then this would indeed

Figure 13

Plots of $[N]$ vs 't' for Various $[C_2D_4]_0$

at $P_{N_2} = 0.63$ Torr

(cf. Table 5 in Appendix)

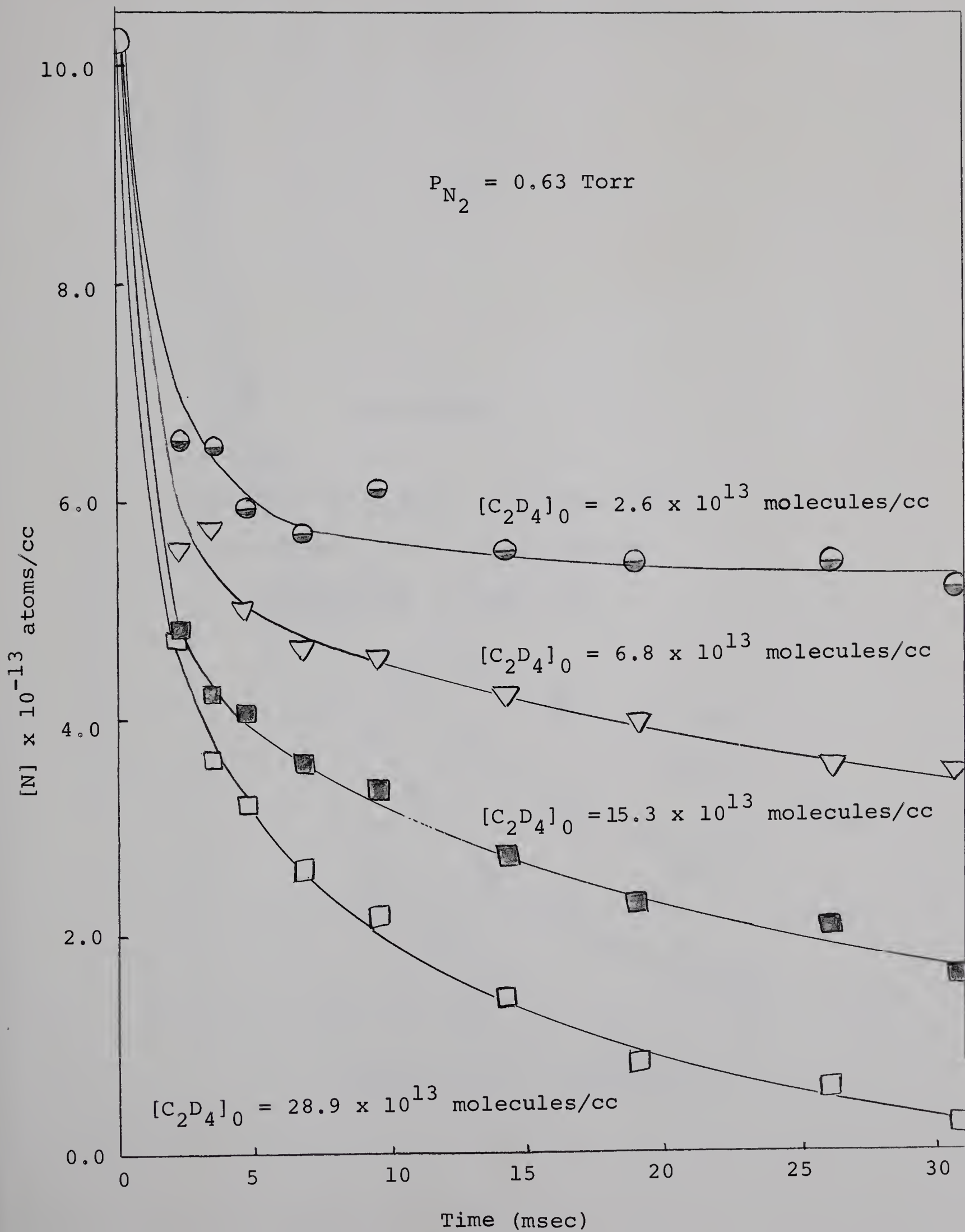


Figure 14

Plots of $[N]$ vs $[C_2D_4]_0$ for Various
Reaction Times at $P_{N_2} = 0.63$ Torr
(cf. Table 6 in Appendix)

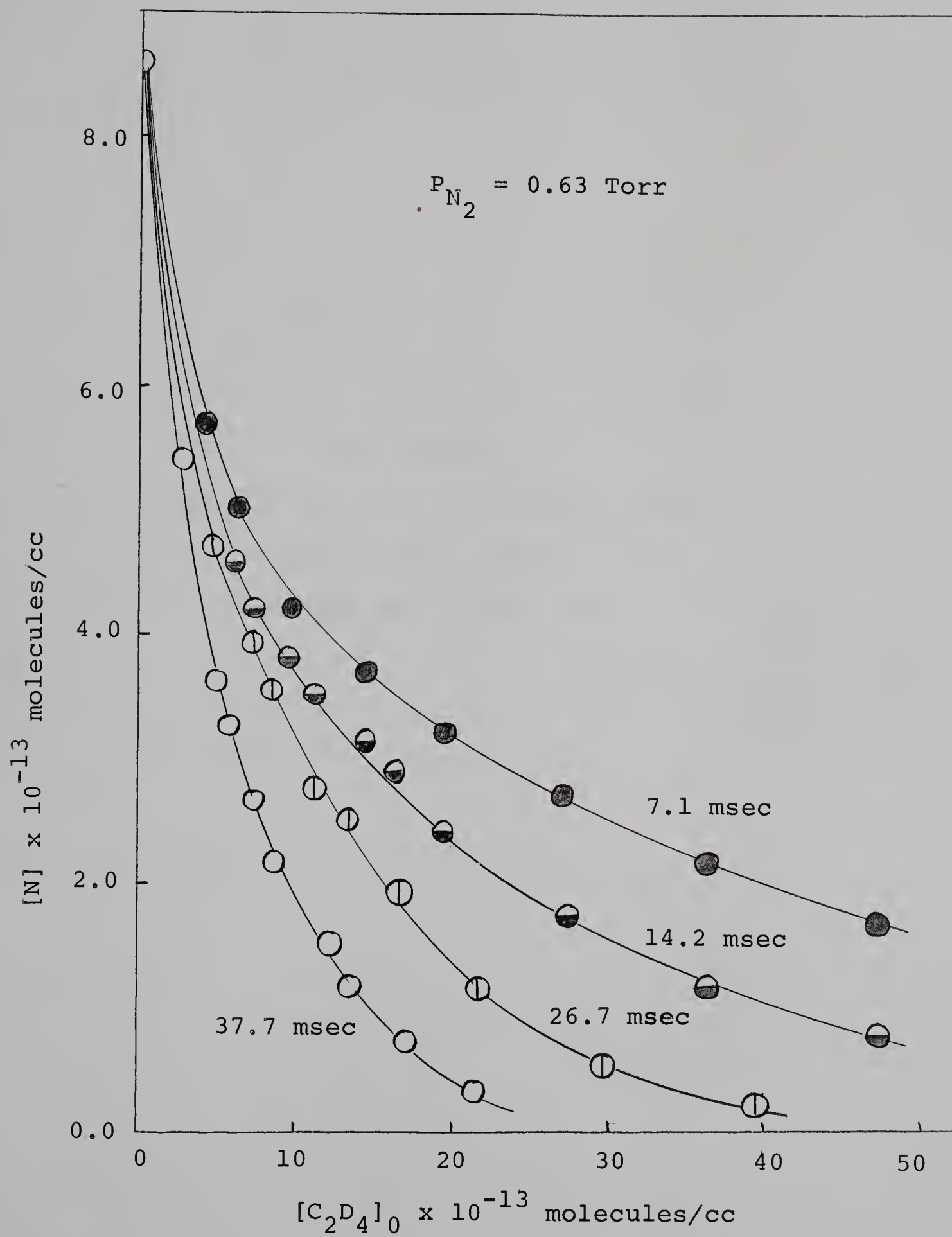
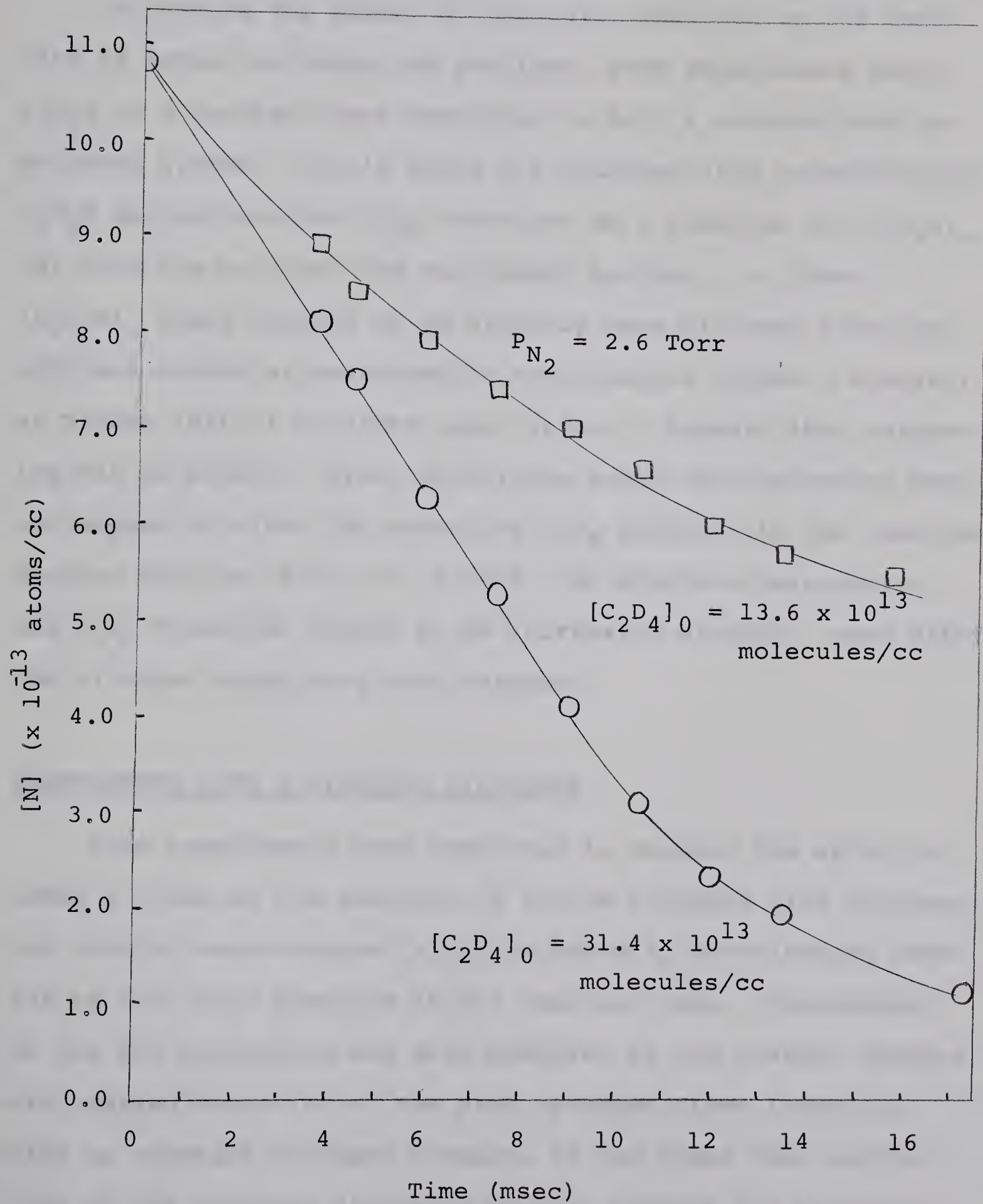


Figure 15

Plots of $[N]$ vs 't' for Two $[C_2D_4]_0$

at $P_{N_2} = 2.6$ Torr

(cf. Table 7 in Appendix)



show the presence of D atoms. It was found that C_2D_4 was in fact formed in the reaction of nitrogen atoms with C_2D_3H .

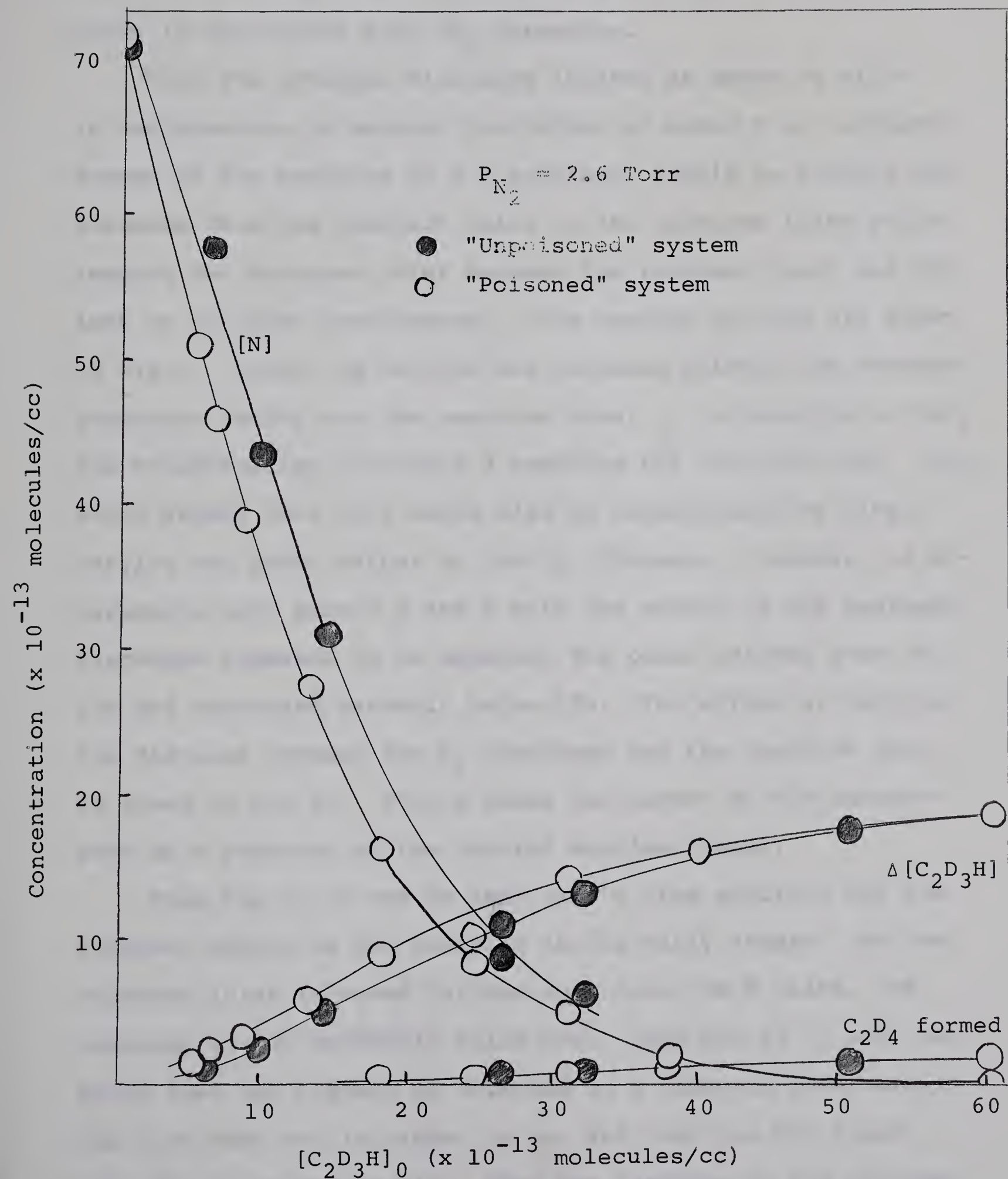
To examine the effect of the wall condition on the reaction of active nitrogen and ethylene, some experiments using C_2D_3H as a reactant were conducted in both a poisoned and unpoisoned system. Fig.16 shows the nitrogen atom concentration, C_2D_3H destruction and C_2D_4 formation as a function of $(C_2D_3H)_0$, for both the poisoned and unpoisoned systems. At lower $(C_2D_3H)_0$ there appears to be slightly more nitrogen atoms and ethylene molecules destroyed in the poisoned system. However, at higher initial ethylene input rates it appears that poisoning has no effect. Also, it will be noted that poisoning does not appear to alter the amount of C_2D_4 produced in the reaction. Another feature of Fig.16 is that the ethylene destruction and C_2D_4 formation appear to be increasing slightly, even after the nitrogen atoms have been consumed.

EXPERIMENTS WITH A HYDROGEN DISCHARGE

Some experiments were conducted to examine the effect of added H atoms on the reaction of active nitrogen with ethylene. Our results were obtained with the added H_2 contributing about 25% of the total pressure in the reaction zone. Enhancement of the HCN production was also observed in our system, coupled with marked depletion of the pink cyanogen flame intensity. With no reactant ethylene present, it was found that initiation of the hydrogen discharge greatly reduced the afterglow

Figure 16

Plots of $[N]$, $\Delta[C_2D_3H]$ and $[C_2D_4]$ Formation
as a Function of $[C_2D_3H]_0$ for "Poisoned" and
"Unpoisoned" Systems at $P_{N_2} = 2.6$ Torr
(cf. Table 8 in Appendix)



intensity and depleted the nitrogen atom concentration by ca. 40%. Also, mass spectral peaks at $m/e = 17, 16, 15$ arose, which is consistent with NH_3 formation.

With the hydrogen discharge located as shown in Fig.4 it was possible to examine the effect of added H at different stages of the reaction of N + ethylene, simply by varying the distance from the reactant inlet to the hydrogen inlet while keeping the hydrogen inlet between the reactant inlet and the leak to the mass spectrometer. The results of this are shown in Fig.17. Also, by varying the distance between the hydrogen resonance cavity and the reaction zone, it is possible to vary the concentration of atomic H reaching the reaction zone. One would expect that this could also be accomplished by simply varying the power output to the H_2 discharge. However, in experiments with atomic N and H only the effect of the hydrogen discharge appeared to be constant for power outputs over ca. 25% and decreased markedly below 25%. The effect of varying the distance between the H_2 discharge and the reaction zone is shown in Fig.18. Fig.19 shows the extent of HCN enhancement as a function of the initial ethylene input.

From Fig.17 it can be seen that H atom addition has the greatest effect on the reaction in its early stages. As the reactant inlet is moved further away from the H inlet, the increase in HCN gradually falls off. From Fig.19 it will be noted that the plateau is attained at a somewhat lower ethylene flow rate and is higher by ca. 20% than the HCN yield when the discharge is off. When the distance of the hydrogen

Figure 17

Plot of Change in HCN Production as a Function of the
Distance Between the Hydrogen Inlet and the Reactant Inlet
(cf. Table 9 in Appendix)

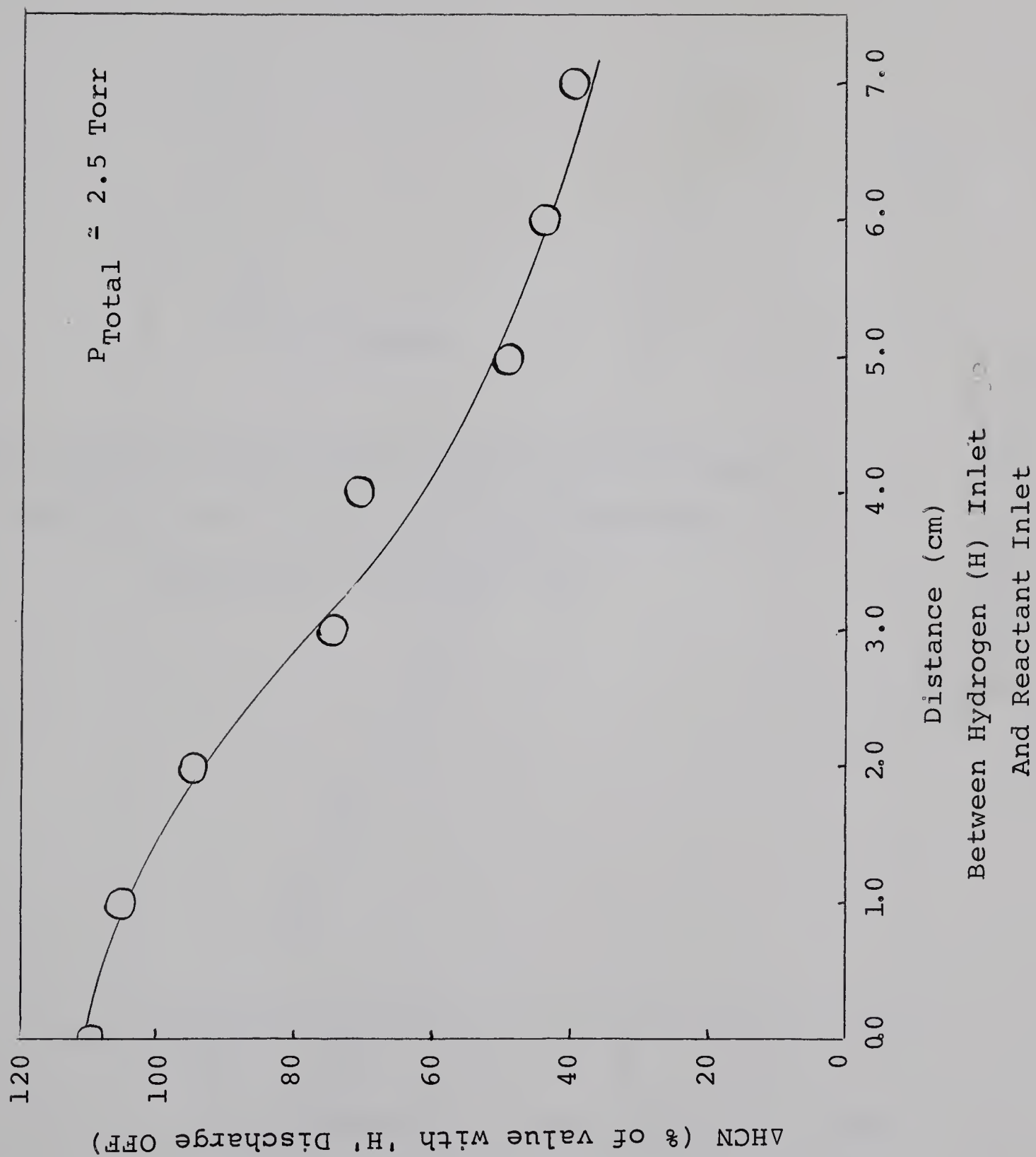


Figure 18

Dependence of ΔHCN on the Distance Between the
Hydrogen Discharge and the Reaction Zone
(cf. Table 10 in Appendix)

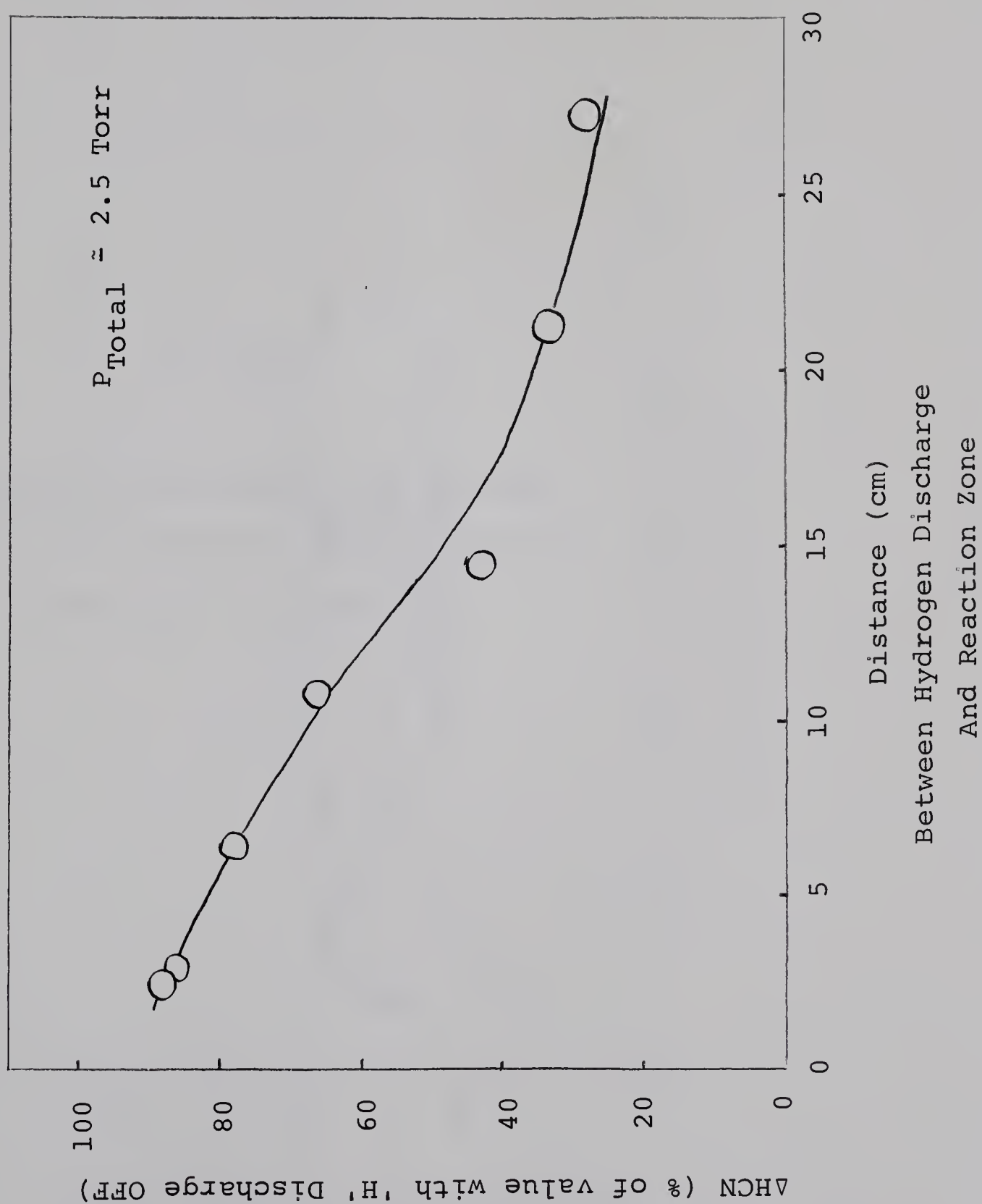
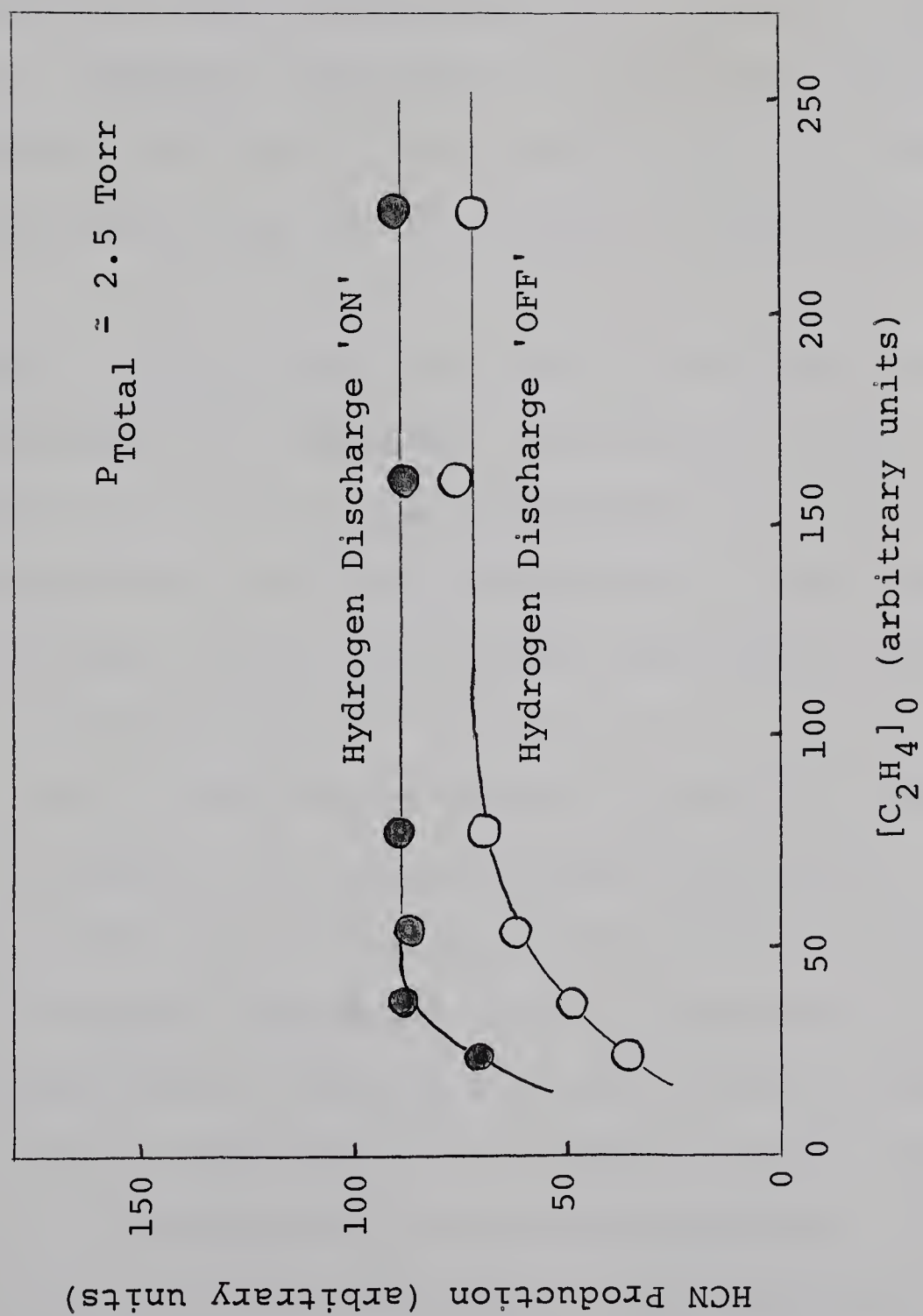


Figure 19

Plot of HCN Production vs $[C_2H_4]_0$
with the Hydrogen Discharge ON and OFF
(cf. Table 11 in Appendix)



discharge from the reaction chamber is varied it is possible to observe how a variation in the number of H atoms entering the reaction zone affects the HCN yield. The greatest increase in HCN is obtained for the largest concentration of H atoms entering the reaction tube.

DISCUSSION

The ionization efficiency curves and the relationship between the afterglow intensity and the square of the ion current, shown in Figures 11 and 12, clearly show the presence of (4S) N atoms in our system. For the experiments performed at 0.63 Torr total pressure, the partial pressure of N atoms was about 3×10^{-3} Torr. Therefore the nitrogen stream was approximately 0.2% dissociated. For the 2.6 Torr results, the nitrogen stream was about 0.4% dissociated for the highest N atom concentration employed.

Metastable nitrogen atoms have been shown to be present in discharged nitrogen^{19,65}. However, since they are only about 0.2% as abundant as (4S) N a few milliseconds after the discharge,⁶⁵ they are believed to be unimportant in our system, where the activated nitrogen has decayed for some 70 msec before entering the reaction zone.

The fact that vibrationally excited N_2 in its ground electronic state is present in active nitrogen originating from an electrodeless discharge, is well established.^{10,67} About 30% of the molecular nitrogen downstream from the discharge is in its first vibrational level. That some of the nitrogen molecules are in higher vibrational levels is evidenced by the work of Starr,⁶⁸ in which excitation of the sodium resonance lines by vibrationally excited N_2 was observed. Vibrationally excited nitrogen may be effectively removed from the system by the insertion of a glass wool plug between the discharge and the

reaction tube.¹¹ Although such a plug was not used in our system, the concentration of N_2 with sufficient vibrational energy to induce chemical change, is believed to be negligible in comparison to other reactive species.

The presence of $A^3\Sigma_u^+ N_2$ must also be considered. In experiments utilizing the reaction of active nitrogen with NH_3 , Dunford¹⁴ found his data to be consistent with the postulate of formation of A state molecules in the discharge and subsequent first order decay along the reaction tube. A logarithmic plot of the extent of NH_3 destruction vs decay time yielded an apparent half life of 0.09 sec for the A state. However, Brennan and Kistiakowsky⁶⁹ show that Dunford's data are also consistent with the postulate of formation of $A^3\Sigma_u^+ N_2$ solely from atom recombination and, within about 1 msec, subsequent deactivation on the wall. Furthermore, with the latter interpretation, Dunford's data indicate that nearly all atom recombinations lead to $A^3\Sigma_u^+ N_2$ formation. The implication is that the NH_3 reaction with active nitrogen, rather than representing a means of titrating for A state molecules at any one point in the reaction tube, represents a measure of the total number of A state molecules generated between the point of NH_3 addition and the quenching trap. By use of the suggestions by Brennan and Kistiakowsky, we may calculate an upper limit for the concentration of A state molecules in our system. If all recombinations result in the formation of A state molecules, and if the molecules survive for 10^{-3} sec, then the steady-state concentration of A state molecules,

$[N_2^*]$, may be represented by

$$[N_2^*] = \frac{k [N]^2 [M]}{k'} \quad (49)$$

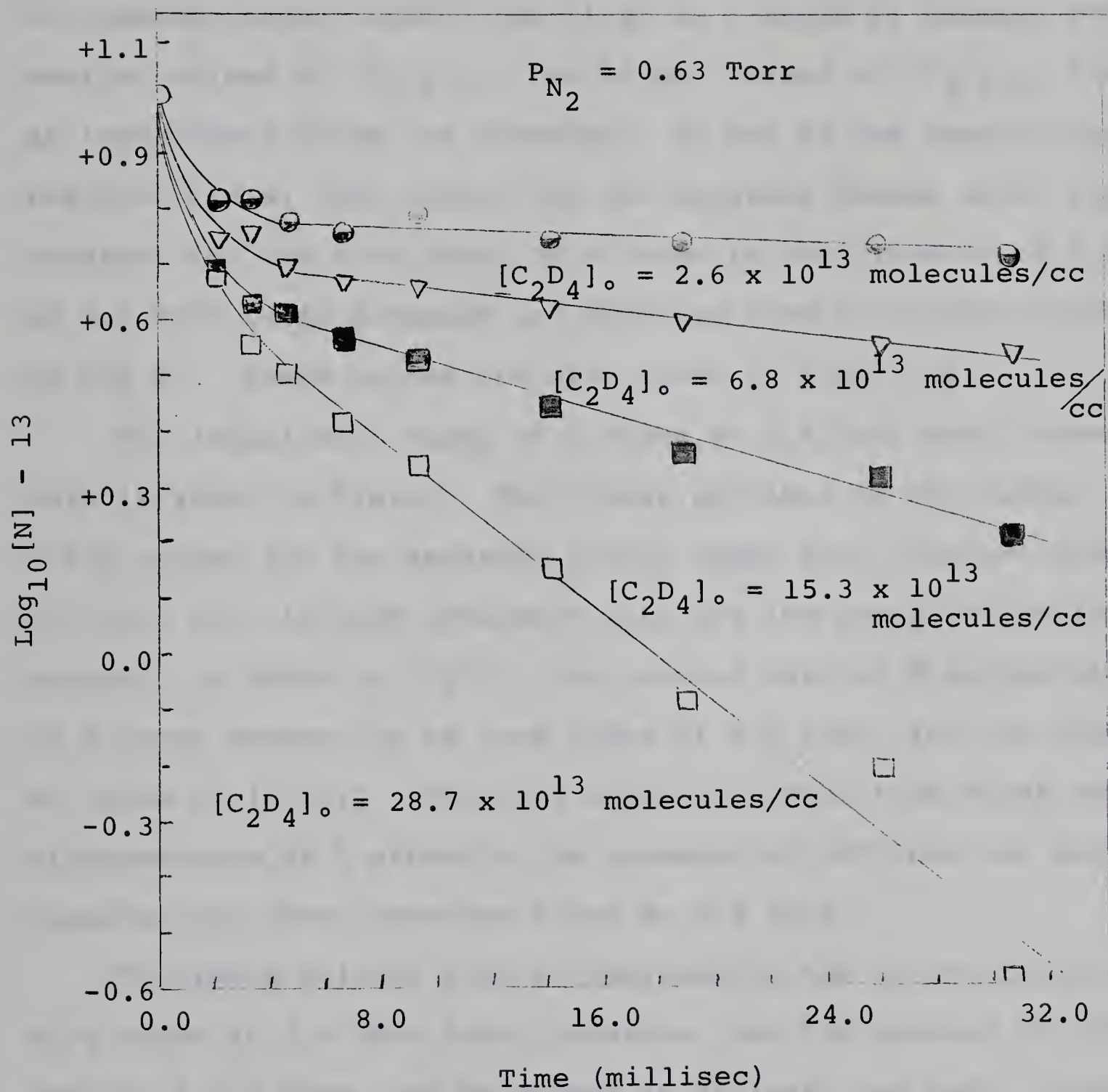
where k is the third order rate constant for N atom recombination and k' is the first order rate constant for wall decay of $A^3\Sigma_u^+ N_2$. Now, k is about 10^{-32} cc² molecules⁻²/sec,⁵ and $k' = 10^3$ sec⁻¹.⁶⁹ Values of $[N] = 5 \times 10^{14}$ atoms and $[M] = 10^{17}$ molecules/cc are typical for our system. Substituting we obtain $[N_2^*] \approx 3 \times 10^{11}$ molecules/cc. We may therefore conclude that $A^3\Sigma_u^+ N_2$ is probably less than 0.1% as abundant as (⁴S) N atoms in our system.

Since pink active nitrogen was not observed, ionic species are believed not to be present in significant amounts. The considerations which follow then pertain to active nitrogen exhibiting the normal Lewis-Rayleigh afterglow, which is believed to contain only (⁴S) N atoms and traces of $A^3\Sigma_u^+$ nitrogen molecules, as potential chemically reactive species.

The rates of decay of N atoms at 0.63 Torr total pressure for different rates of input of C₂D₄, shown in Fig.13 may be plotted logarithmically as in Fig.20. A feature of these plots is the transition, at a reaction time of ca. 4 msec, from a decay process of apparent order greater than one to apparent first order in nitrogen atoms. Since the C₂D₄ decomposition is less than 13% of the initial concentration of ethylene-d₄ the slopes of the linear portions of the four plots may be divided by the appropriate values of $[C_2D_4]_0$ and multiplied by 2.303 to obtain four values of an apparent second order rate

Figure 20

Plot of $\text{Log}[N]-13$ vs 't' at $P_{N_2} = 0.63$ Torr
(cf. Table 5 in Appendix)



constant. These are shown in the Table 12A. The decay of N atoms as a function of $[C_2D_4]_0$ from Fig.14 may also be plotted logarithmically to give Fig.21. A slight but discernible trend to apparent order higher than first in N atoms is present for smaller values of $[C_2D_4]_0$. For higher values of $[C_2D_4]_0$, linear logarithmic plots are observed. By use of the appropriate reaction times, four values for the apparent second order rate constant for the rate decay of N atoms in the presence of C_2D_4 at 0.6 Torr total pressure are obtained from the linear plots of Fig.21. These values are also given in Table 12B.

The logarithmic decay of N atoms at 2.6 Torr total pressure is shown in Fig.22. The linear portions of the curves yield values for the apparent second order rate constant shown in Table 12C, in good agreement with the low pressure results. However, as shown in Fig.22, the initial rate of disappearance of N atoms appears to be zero order at 2.6 torr, for the higher value of $[C_2D_4]_0$. Thus the apparent higher than first order disappearance of N atoms in the presence of ethylene was only observed for short reaction times at 0.6 Torr.

The rapid initial rate of decrease in the concentration of N atoms at 0.6 Torr total pressure, and the absence of this effect at 2.6 Torr, can be viewed in at least two ways. First, if there were back diffusion of the ethylene upon entering the reaction chamber the point of zero reaction time would be effectively shifted upstream. Since back diffusion would be more important at high $[C_2D_4]_0$, then the deviation from pseudo first order behaviour would be greatest for high $[C_2D_4]_0$. The

Figure 21

Plot of $\text{Log}[N]-13$ vs $[\text{C}_2\text{D}_4]_0$ at $P_{\text{N}_2} = 0.63$ Torr
(cf. Table 6 in Appendix)

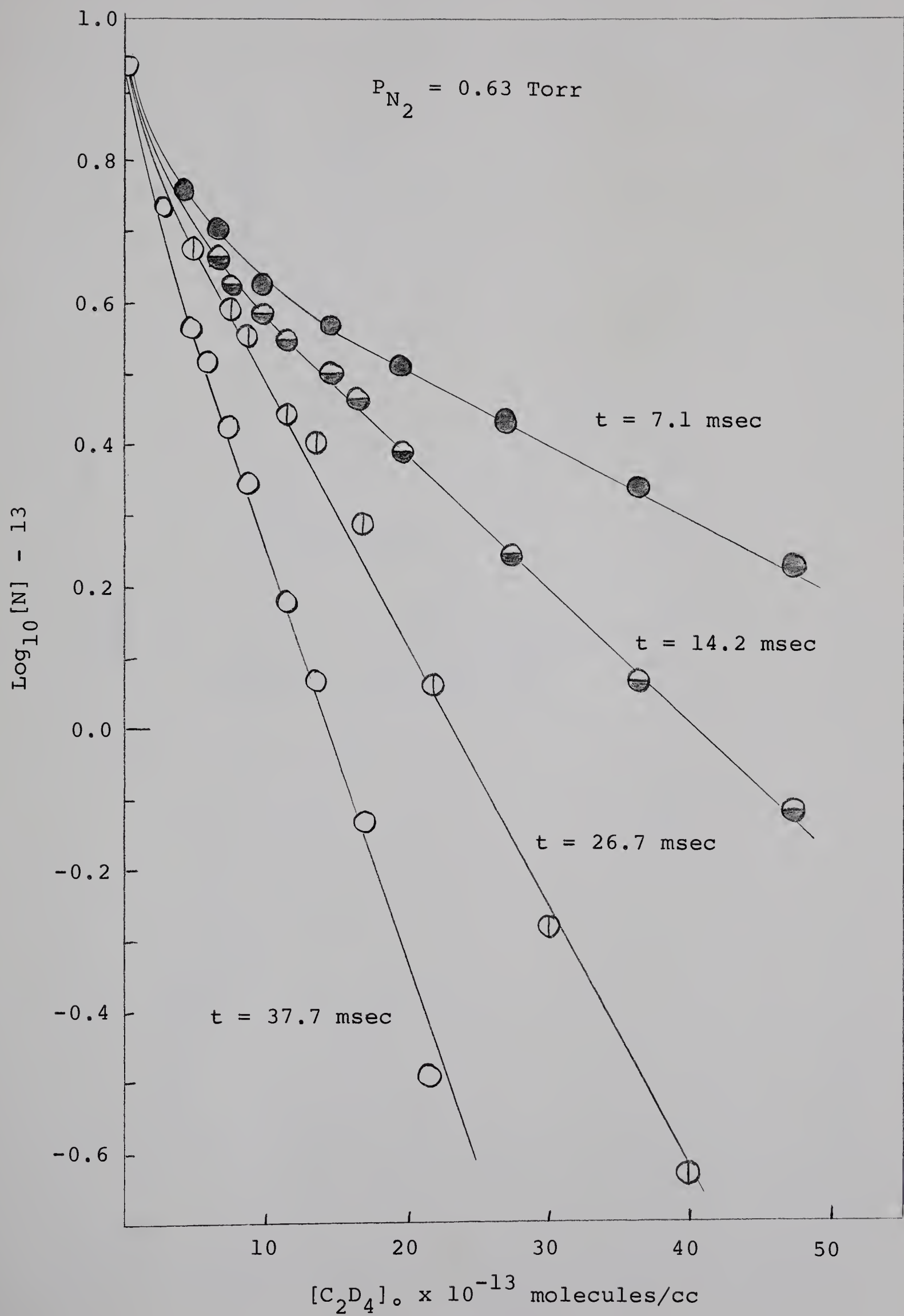
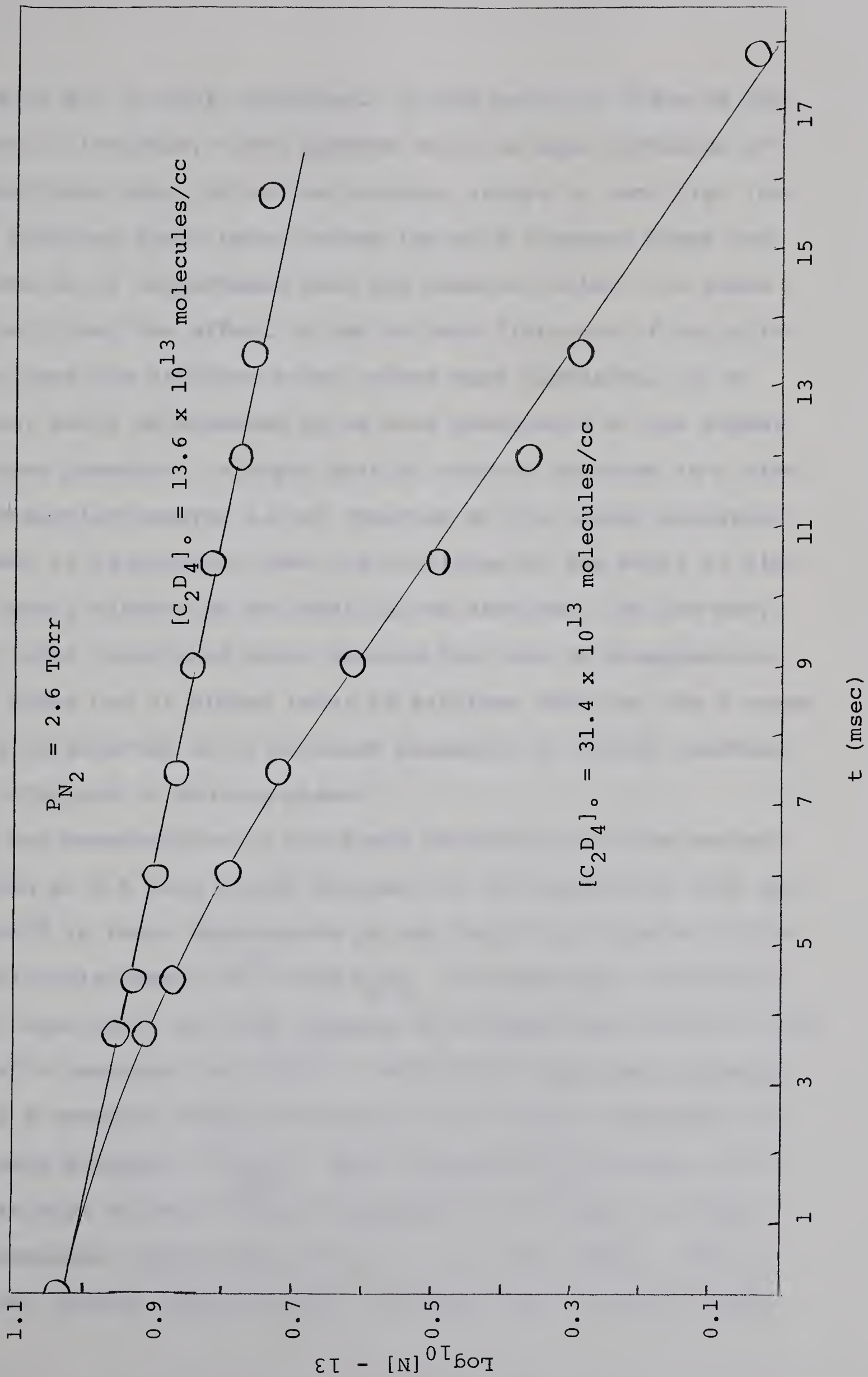


Figure 22

Plot of $\text{Log}[N]-13$ vs 't' at $P_{N_2} = 2.6$ Torr
(cf. Table 7 in Appendix)



opposite is, in fact, observed. If the reaction flame is observed in the dark, there appears to be no back diffusion of the ethylene into the active nitrogen except at very high initial ethylene input rates, where the pink cyanogen flame can be seen ca. 1 cm upstream from the reactant inlet. It seems unlikely that the effect is due to back diffusion of the nitrogen into the ethylene inlet, since back diffusion, if it occurs, would be expected to be more pronounced at the higher nitrogen pressure. A rapid initial rate of decrease in N atom concentration however is not observed at the higher pressure. Second, it is possible that the condition of the walls is significantly altered by the addition of ethylene. At low ethylene input rates this could enhance the rate of disappearance of N atoms but at higher rates of ethylene addition the N atoms would be expected to be depleted primarily by direct reaction with ethylene in the gas phase.

Our observations on the rapid decrease in N atom concentration at 0.6 Torr may be relevant to the results of Back and Fersht³⁸ in their experiments on the reaction of active nitrogen with mixtures of $N^{15}O$ and C_2H_4 . As mentioned previously, they found that as small amounts of ethylene were added to the $N + N^{15}O$ reaction, the $[N^{14}N^{15} + HCN]$ yield decreased markedly until a constant value was obtained for further increases in the mole fraction of C_2H_4 . They attributed this result to a competition between $N^{15}O$ and ethylene for $A^3\Sigma_u^+ N_2$, in which the ethylene reacted about five to ten times faster, and yet did not undergo decomposition. However Back's results could

also be due to a marked depletion of the N atom concentration, for small amounts of added ethylene, an effect observed directly in our system.

The results of experiments using C_2D_3H as a reactant in the "poisoned" and "unpoisoned" systems at 2.6 Torr and shown in Fig.16 may be plotted logarithmically as in Fig.23. Values of the apparent second order rate constant are reported in Table 12D and agree reasonably well with the previous values for the apparent rate constant. Although linear portions of the logarithmic plots appear to be parallel, yielding the same apparent second order rate constant, it will be noted that in the "unpoisoned" system there appears to be slightly less N and C_2D_3H destroyed than in the "poisoned" system at low $[C_2D_3H]_0$.

There are various possible explanations for the generation of C_2D_4 in the reaction of active nitrogen with C_2D_3H . A plausible intermediate for C_2D_4 formation would appear to be the ethyl radical which requires D atom addition to C_2D_3H for its formation. Abstraction of the H atom from C_2D_4H by an N atom (analogous to Herron's reaction (5)⁴⁰) or by a deuterium atom could occur. However, the abstraction reaction, particularly by an N atom, would require a significant activation energy. Since hot ethyl radicals are believed to be rapidly collisionally deactivated,⁴⁴ they would probably be thermalized before encountering an N or D atom. Therefore, the simple exchange reaction

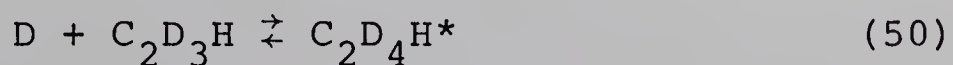
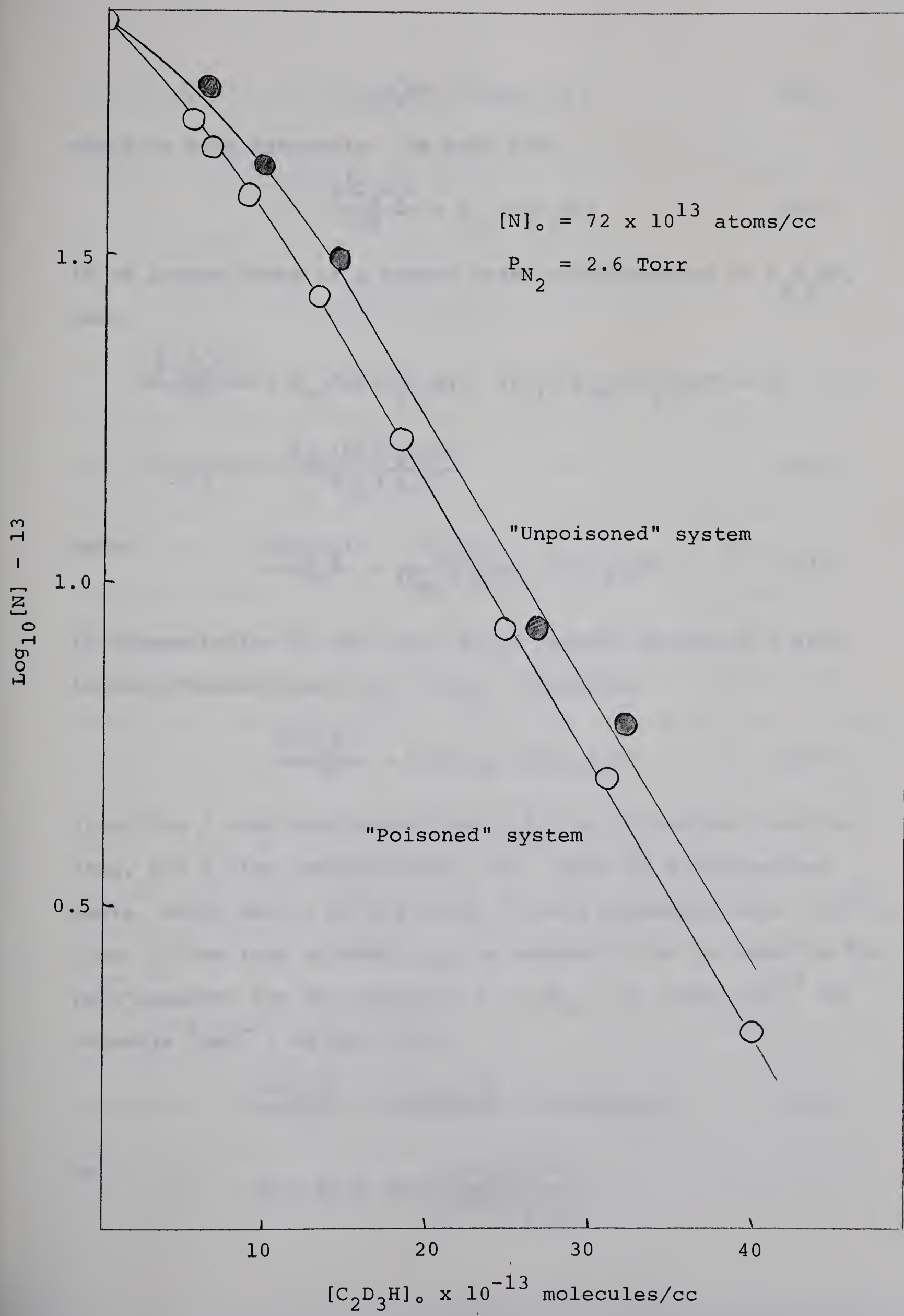
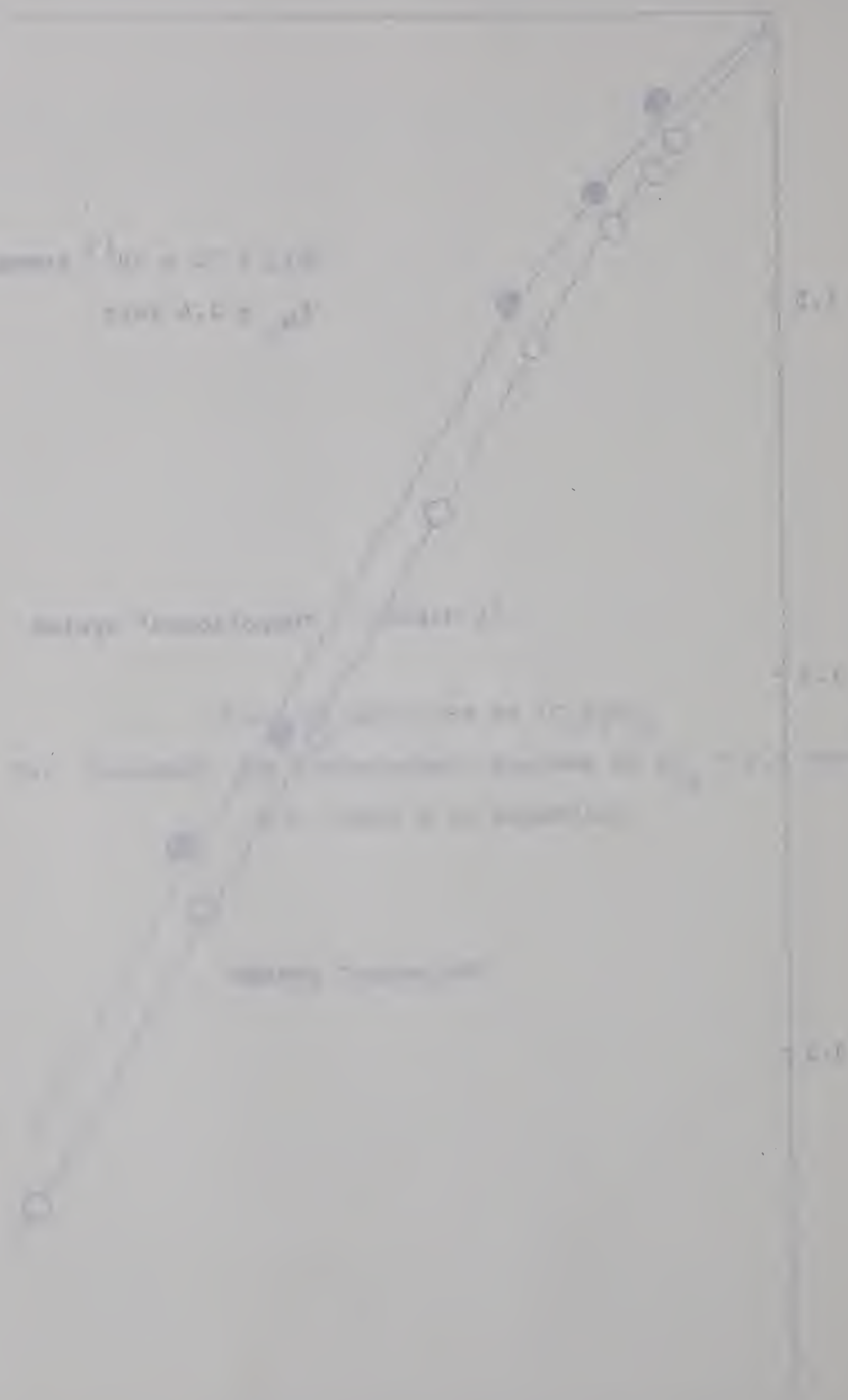


Figure 23

Plot of $\text{Log}[N]-13$ vs $[\text{C}_2\text{D}_3\text{H}]_0$
for "Poisoned" and "Unpoisoned" Systems at $P_{\text{N}_2} = 2.6$ Torr
(cf. Table 8 in Appendix)



$\log_{10} \frac{P}{P_0} = \frac{2\pi^2}{\lambda^2} \Delta \rho$
 $\Delta \rho = 0.1 \text{ g/cm}^3$





might be more favorable. We note that

$$\frac{d[C_2D_4]}{dt} = k_{51}[C_2D_4H^*] \quad (52)$$

If we assume there is a steady state concentration of $C_2D_4H^*$, then

$$\frac{d[C_2D_4H^*]}{dt} = k_{50}[D][C_2D_3H] - (k_{51} + k_{50})[C_2D_4H^*] = 0$$

$$\therefore [C_2D_4H^*] = \frac{k_{50}[D][C_2D_3H]}{(k_{51} + k_{50})} \quad (53)$$

Hence

$$\frac{d[C_2D_4]}{dt} = \frac{k_{50}k_{51}}{(k_{50} + k_{51})} [D][C_2D_3H] \quad (54)$$

If fragmentation of the "hot" ethyl radical occurs in a statistical fashion then $k_{50} = 4k_{51}$. Therefore

$$\frac{d[C_2D_4]}{dt} = 1/5 k_{50} [D][C_2D_3H] \quad (55)$$

Since the D atom originates from C_2D_3H in an earlier reaction step, the D atom concentration, $[D]$, again on a statistical basis, would be 3/4 of the total H and D concentrations, $[D+H]$. Also, if the rate constant k_{50} is assumed to be the same as the rate constant for the reaction $H + C_2H_4$, i.e. about 10^{-13} cc molecule⁻¹sec⁻¹, we may write

$$\frac{d[C_2D_4]}{dt} = \frac{3 \times 10^{-13}}{5 \times 4} [D+H][C_2D_3H] \quad (56)$$

or

$$[D+H] = 20/3 \frac{d[C_2D_4]/dt}{10^{-13}[C_2D_3H]}$$

If we approximate $d[C_2D_4]/dt$ by

$$\frac{d[C_2D_4]}{dt} \approx \frac{C_2D_4 \text{ formed}}{\text{total reaction time}} = \frac{2 \times 10^{13}}{0.02} = 10^{15} \text{ molecules/cc/sec} \quad (57)$$

with $[C_2D_3H]_0 = 6 \times 10^{14} \text{ molecules/cc}$, then

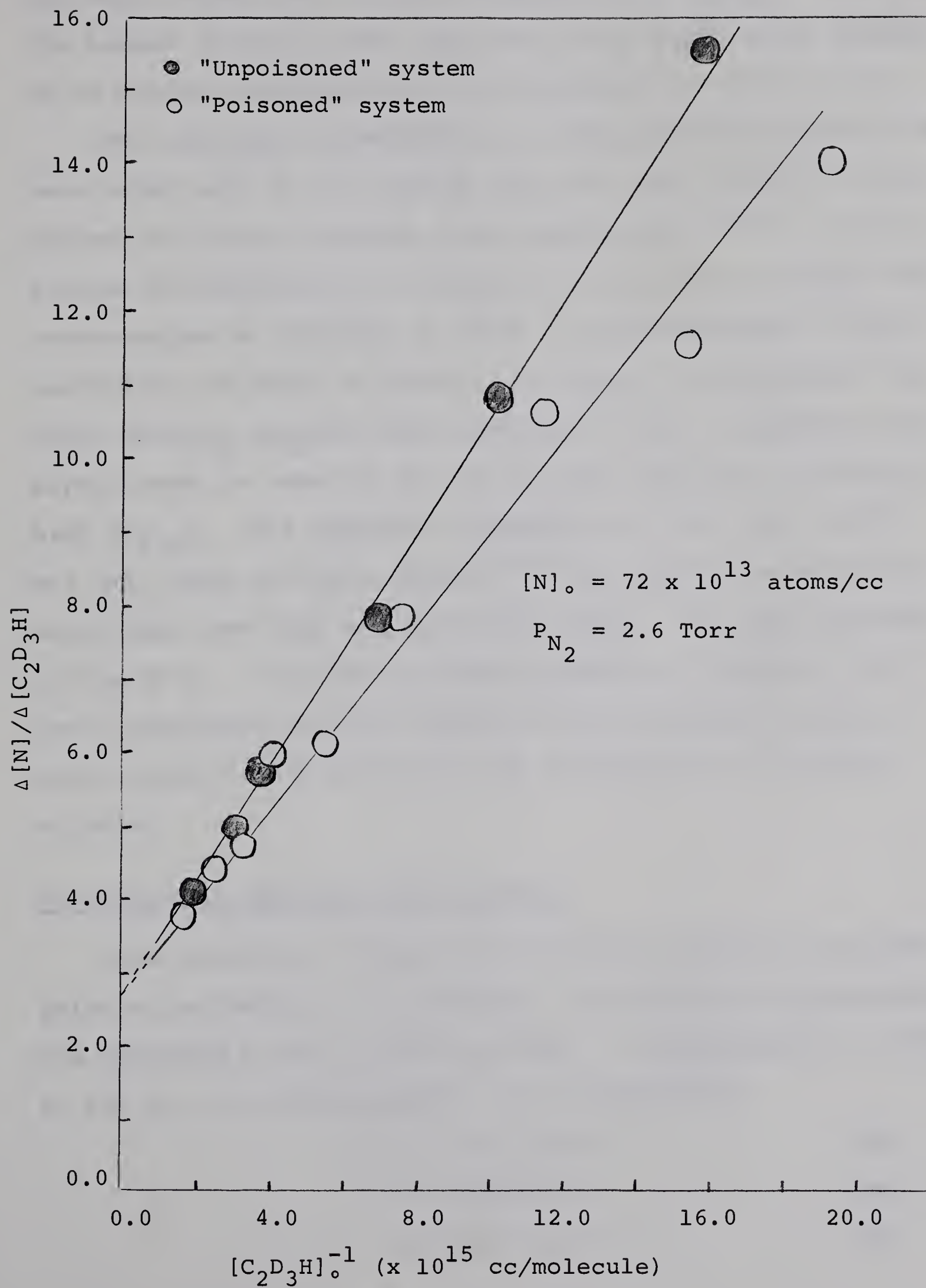
$$[D + H] \approx 20/3 \frac{10^{15}}{10^{-13} (6 \times 10^{14})} = 10^{14} \text{ atom/cc} \quad (58)$$

This is roughly 1/7 of the initial nitrogen atom concentration. However, Turner and Cvetanovic⁴³ have shown that there is a considerable isotope effect in the reaction of H and D atoms with C_2D_4 and C_2H_4 , respectively. They found that there was no isotopic exchange in the reaction $H + C_2D_4$ but there was isotopic exchange in the reaction $D + C_2H_4$. Their results showed that in the decomposition of the "hot" ethyl radical, a C-H split occurs preferentially to a C-D split (aside from statistical considerations). The value 10^{14} above should therefore be interpreted as an upper limit, since the decomposition of $C_2D_4H^*$ to $C_2D_4 + H$ would occur more often than would be expected purely on statistical grounds and also since we have assumed all $C_2D_4H^*$ decompose in reactions (-50) and (51). The statistical factor would be $> 3/20$ and hence $[D + H] < 10^{14} \text{ atoms/cc}$.

The data of Fig.16 can be used to show the dependence of the number of nitrogen atoms destroyed per ethylene molecule destroyed, $\Delta N/\Delta C_2D_3H$, on the initial ethylene input rate, as shown in Fig.24. The ratio is highest at low $[C_2D_3H]_0$ and is apparently proportional to $[C_2D_3H]_0^{-1}$. Herron has found that

Figure 24

Plot of $\Delta[N]/\Delta[C_2D_3H]$ vs $[C_2D_3H]_0^{-1}$ for
"Poisoned" and "Unpoisoned" Systems at $P_{N_2} = 2.6$ Torr
(cf. Table 8 in Appendix)



the ratio $\Delta N/\text{HCN}$ has a similar dependence on $[\text{C}_2\text{H}_4]_0$. Even at the highest $[\text{C}_2\text{D}_3\text{H}]_0$ used, the ratio of nitrogen atoms destroyed to ethylene destroyed has not decreased to a value of 2:1.

The catalyzed recombination of nitrogen atoms by ethylene has been ruled out⁴⁰ on the grounds that the ratio $\Delta N/\text{HCN}$ is independent of initial nitrogen atom concentration.^{36,40} We have studied the dependence of $\Delta N/\Delta \text{C}_2\text{D}_4$ on the initial nitrogen atom concentration as reported in Table 13 and have found a linear correlation as shown in Fig. 25. As $[\text{C}_2\text{D}_4]_0$ is increased, the ratio $\Delta N/\Delta \text{C}_2\text{D}_4$ becomes less dependent on $[\text{N}]_0$. Therefore catalysis seems to occur at low $[\text{C}_2\text{D}_4]_0$ but tends not to occur at high $[\text{C}_2\text{D}_4]_0$. The apparent independence of the ratio $\Delta N/\text{HCN}$ and $[\text{N}]_0$ found by other workers^{36,40} can readily be explained since they used high ethylene input rates. That the intercept in Fig. 25 is > 3 , provides strong evidence in support of Herron's conclusion that the extent of HCN production is not a valid measure of the nitrogen atom concentration in active nitrogen.

The Effect of Hydrogen Atom Addition

When molecular nitrogen and molecular hydrogen are mixed prior to activation in a discharge, as in Herron's experiments, the resulting N and H atoms may decay independently to reform N_2 and H_2 , or interdependently via the processes

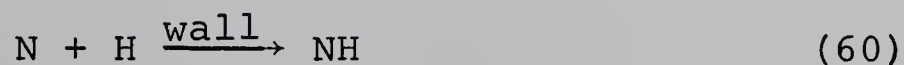
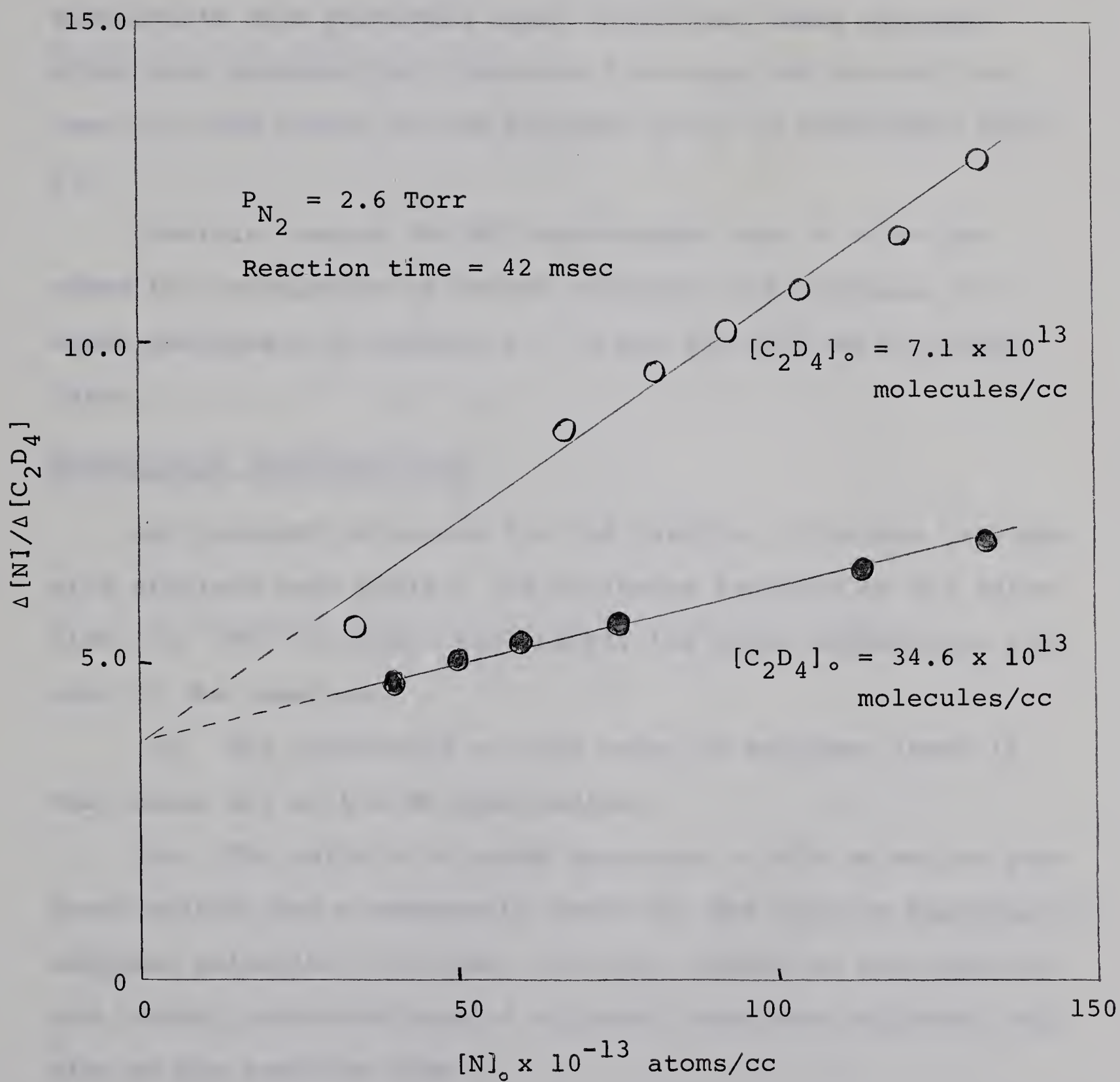


Figure 25

Plot of $\Delta[N]/\Delta[C_2D_4]$ vs $[N]_0$ at $P_{N_2} = 2.6$ Torr
(cf. Table 13 in Appendix)



Subsequent reactions of surviving NH radicals could lead to the formation of traces of NH_3 . The reactions (59, 60 and 42) are known to occur and lead to N atom destruction. Our experiments were performed under conditions where hydrogen atoms were produced in a separate discharge and entered the reaction zone either at the ethylene inlet or downstream from it.

Possible reasons for HCN enhancement when H atoms are added to the reaction of active nitrogen with ethylene, as shown previously in Figures 17, 18 and 19, will be discussed later.

Mechanistic Considerations

Any proposed mechanism for the reaction of active nitrogen with ethylene must explain the following features of the reaction: (a) HCN is almost exclusively the major condensible product of the reaction.

(b) HCN production at high rates of ethylene input is only about 2/3 of the NO destruction.

(c) The ratio of N atoms destroyed to HCN molecules produced $\Delta\text{N}/\text{HCN}$, and a comparable quantity, the ratio N destroyed to ethylene molecules destroyed, $\Delta\text{N}/\Delta\text{C}_2\text{H}_4$, depend on the ratio of the initial concentrations of nitrogen atoms and ethylene, and also on the reaction time.

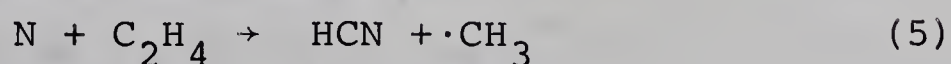
(d) H atom addition to the reaction mixture enhances the HCN production.

(e) At a pressure of 2.6 Torr, poisoning of the system

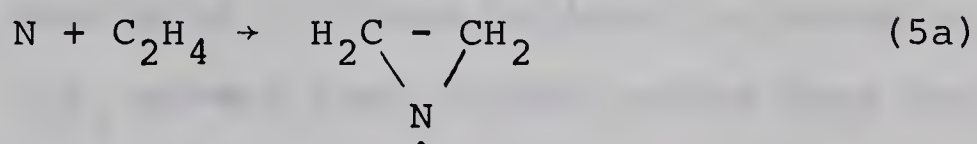
increases both the N atom destruction and the ethylene destruction at low ethylene input rates but appears to have no effect at high rates of ethylene input.

On the Primary Reaction Step

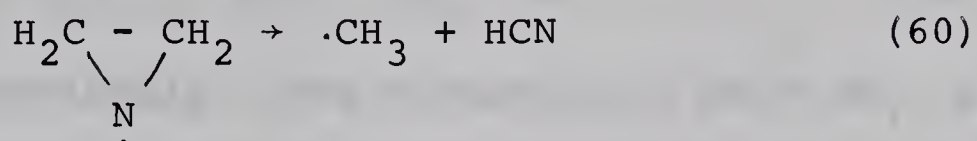
The primary reaction step in the reaction of active nitrogen with ethylene has been believed to be



primarily on energetic grounds albeit the step violates conservation of spin and requires a hydrogen atom migration. It has also been proposed⁷¹ that reaction (5) might occur via formation of a complex resembling ethyleneimine



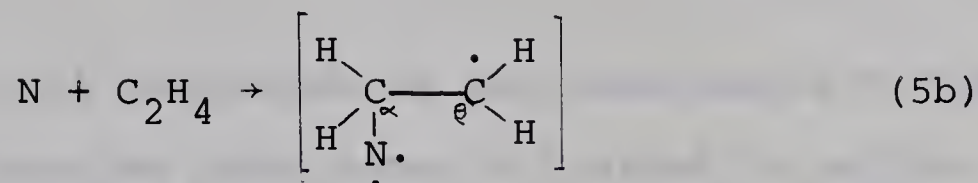
which subsequently undergoes the decomposition reaction



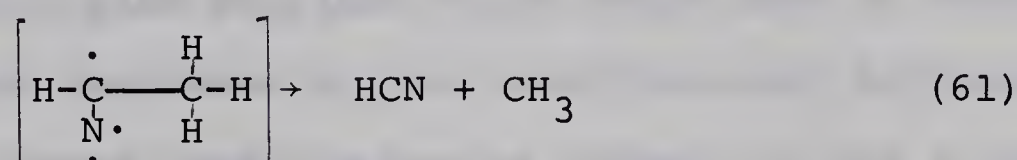
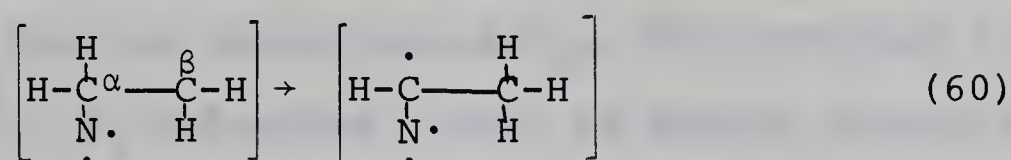
The latter reaction (60) involves a drastic rearrangement of the ethylene-nitrogen atom complex.

With triplet NH radicals⁵² and triplet CH₂ radicals, the initial interaction with olefin appears to be the formation of a biradical. Evidence for the biradical intermediate in the methylene radical case is the lack of stereospecificity in the reaction of triplet methylene radicals with cis butene-2.⁷² Both cis and trans 1,2 dimethylcyclopropane are formed. By analogy, the initial interaction of N with C₂H₄ might be expected

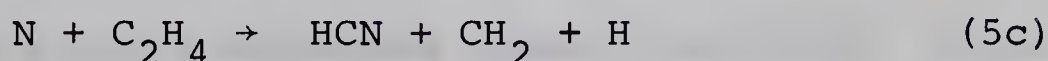
to conserve spin by the formation of a triradical intermediate viz.



This could be followed by hydrogen atom migration from the alpha carbon atom to the beta carbon atom (C_α to C_β) and subsequent decomposition to HCN and CH_3 .



These reactions are analogous to those believed to occur in the attack of NH on C_2H_4 except that in the latter case the migration of H is from N to C_β . The reaction



is not favored energetically. The formation of $\text{CN} + \text{CH}_4$, although energetically favorable, apparently does not occur since methane is found only in trace amounts as a product of the reaction

The intermediate formed in reaction (60) $\text{H}-\overset{\cdot}{\underset{\text{N} \cdot}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$, might be expected to decompose partly via C-H bond rupture to form $\text{CH}_3\text{CN} + \text{H}$, even though C-C rupture would be favored. While CH_3CN is a minor product of the reaction, its mode of formation has not been determined. Another possibility is that the tri-radical formed by the initial interaction of a nitrogen atom with ethylene does not undergo H migration but merely ruptures at the C—C bond to form $\text{CH}_2\text{N} \cdot + \cdot \text{CH}_2$. Energetically this

would make the primary step almost thermoneutral but it would conserve spin.

The possibility of initiation of the reaction of N atoms with ethylene by a species other than 4S N atoms in active nitrogen must be considered. Nitrogen in its $A^3\Sigma_u^+$ state appears to be the most likely alternative reactant and, in its lowest vibrational level, possesses about 140 kcal/mole of energy in excess of that of ground state N_2 . The possible initiation step by $A^3\Sigma_u^+$ N_2 molecules, could be energy transfer to ethylene, to form triplet ethylene which could then be consumed by N atoms or could decompose to form acetylene and hydrogen. It should also be noted that the energy content of the A state makes the fragmentation of C_2H_4 to two methylene radicals energetically feasible. If the mode of formation of A state nitrogen is considered however, initiation of the reaction of N atoms with ethylene by A state molecules appears unlikely. Since the formation of A state molecules is believed to result solely from three body atom recombination, both the rate of initiation of the reaction and the overall rate of disappearance of N atoms would be higher than first order in atomic nitrogen. Our results show the reaction to be first order in both N atoms and ethylene.

Competitive Processes in the Reaction of $N + C_2H_4$

At first let us assume that the primary process is in fact represented by $N + C_2H_4 \rightarrow HCN + \cdot CH_3$ followed by the consumption of N atoms by $N + CH_3 \rightarrow HCN + 2H$. We see immediately that

these two reaction steps alone explain the predominance of HCN as the major product but fail to explain any of the other important features of the reaction. If it is assumed that there is a simple catalysis of N atom recombination with ethylene as a third body and the reaction $N + N + C_2H_4 \rightarrow N_2 + C_2H_4$ is added to the above this would explain why all of the N atoms are not consumed quantitatively to form HCN. However this predicts that the rate of nitrogen atom disappearance would be of order greater than one which is not observed. Also H atom addition would have no effect according to this mechanism.

Hydrogen atoms produced in the $N + CH_3$ reaction would probably suffer two possible fates: (a) at very low rates of ethylene input H atoms could recombine in the gas phase or on the surface or (b) at very high rates of ethylene input, H atoms would undoubtedly be consumed directly by ethylene to form "hot" ethyl radicals.

The consumption of H by HCN and by the three body combination with N would be negligibly slow under the experimental conditions involved.

The speed of the wall recombination of H can be obtained from the recombination efficiency, γ , which is defined as the fraction of wall collisions resulting in recombination. For dry Pyrex $\gamma = 6 \times 10^{-3}$ while for moist Pyrex $\gamma = 10^{-5}$.⁷³ If we assume that γ for our system is about 10^{-4} , we may calculate the rate constant for the wall recombination of H atoms to be roughly 13 sec^{-1} . Talrose⁷⁴ has determined the rate of consumption of H atoms by ethylene to be 3.2×10^{-13}

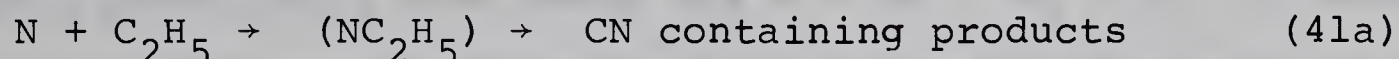
cc-molecule⁻¹sec⁻¹. He notes however, that this value must represent a lower limit, since the extent of the reverse reaction has not been taken into account. Using these data, the ratio of the rates for wall destruction of hydrogen atoms compared to their gas phase addition to ethylene may be calculated to be approximately $10^{14}/[\text{C}_2\text{H}_4]$. The two rates are competitive therefore for ethylene concentrations of the order of 10^{14} molecules/cc. Such a value is typical of the ethylene input rates used in our system.

Subsequent to the above wall reaction, there may be some NH formation from the wall combination of N and H. Since the rate constant for the reaction of NH with ethylene has been estimated to be 10^{-14} cc molecule⁻¹sec⁻¹ ⁵² and since the reaction $\text{N} + \text{NH}$ would be expected to be fast, it is believed that under conditions required for NH formation, subsequent consumption of NH by N atoms would predominate.

We now consider the fate of the "hot" ethyl radicals produced upon the addition of H atoms to ethylene. We may calculate an upper limit for the concentration of this species in the following manner. For the experiments with $\text{C}_2\text{D}_3\text{H}$ as reactant, we have calculated an upper limit for the $[\text{D} + \text{H}]$ to be approximately 10^{14} atoms/cc for a value of $[\text{C}_2\text{D}_3\text{H}]_0 = 6 \times 10^{14}$ molecules/cc, which is the largest rate of ethylene input for these experiments. Using equation (53), assuming k_{50} to be ca. 10^{-13} cc molecule⁻¹sec⁻¹, ⁷⁴ and $(k_{-50} + k_{51})$ to be equal to the rate constant for unimolecular decomposition of C_2H_5^* , 10^7 or 10^8 sec⁻¹, ⁴⁴ we obtain an upper limit for

the concentration of hot ethyl radicals in our system to be about 10^9 molecules/cc. It can be shown on this basis that the hot ethyl radicals would deactivate at a rate comparable to their unimolecular decomposition rate, for the pressures used in our system. It follows that since the hot species undergoes about 10^3 stabilizing collisions before encountering a nitrogen atom, ethyl radicals which may react with N atoms would be thermalized.

Subsequent reactions of the thermalized ethyl radicals which are considered most probable in the present system are (a) reaction with N atoms, (b) reaction with H atoms, and (c) addition to ethylene. The reaction with N atoms would probably be either an initial combination process followed by decomposition



or an abstraction reaction



Since the abstraction reaction would require an activation energy of about 20 kcal, it is believed that the reaction (41a) would predominate at the temperatures used in the present study. It is noteworthy that the photolytic decomposition of ethyl azide, $\text{CH}_3\text{CH}_2\text{N}_3$, which most likely proceeds through the intermediate $\text{CH}_3\text{CH}_2\text{N}$, results in CN containing products.⁵²

The reaction of H with C_2H_5 to form a "hot" ethane molecule is a well known reaction and probably occurs at every collision. The rate constant for this process is believed to be about

four powers of ten higher than the rate constant for the $\text{H} + \text{C}_2\text{H}_4$ reaction.⁷⁵ The fraction of the hot ethane molecules which are "cracked" into two methyl radicals depends upon the rate at which C_2H_6^* is collisionally deactivated. At the pressures used in our system, the cracking process would predominate over the stabilization process. CH_3 produced in the cracking process could then be consumed by atomic nitrogen.

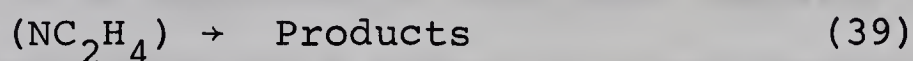
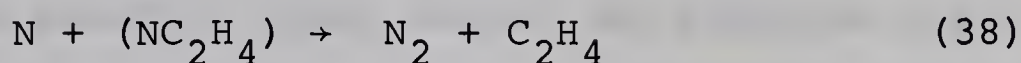
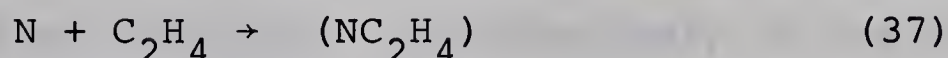
The addition of C_2H_5 to C_2H_4 is known to be a slow reaction,⁷⁶ having an activation energy of some 7 kcal/mole. We therefore conclude that it is not an important reaction step in the overall reaction of N atoms with C_2H_4 .

Possible Modes of N Atom Decay without Ethylene Destruction

As already discussed, the presence of imino radicals provide a route for N atom decay via $\text{N} + \text{NH} \rightarrow \text{N}_2 + \text{H}$. It would appear that N atom combination with H atoms on the wall is a more likely source of NH radicals, than the reaction $\text{N} + \text{C}_2\text{H}_5 \rightarrow \text{NH} + \text{C}_2\text{H}_4$, suggested by Herron.⁴⁰

Another route for N atom destruction without a corresponding destruction of ethylene is a catalyzed recombination of N atoms with ethylene acting as the third body. Preclusion of this route by other workers^{36,40} appears to have been premature. Our Fig.25 shows a linear dependence of $\Delta\text{N}/\Delta\text{C}_2\text{D}_4$ on $[\text{N}]_0$, especially at lower rates of ethylene input. Since the rate of N atom decay does not appear greater than first order in N atoms, it is believed that an (NC_2H_4) complex is formed which has a sufficiently long life that the rate of decay of N atoms can

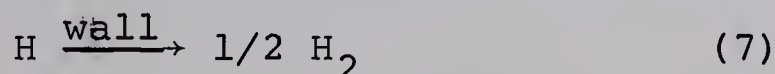
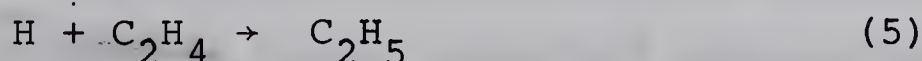
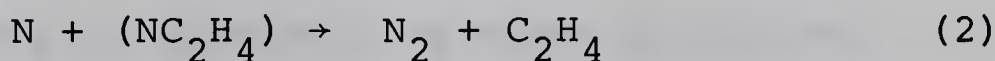
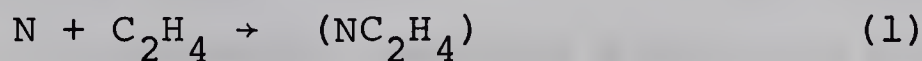
occur by steps which are first order in the concentration of N atoms



Since the catalyzed recombination of N atoms, via the steps (37-39), will account for the observed dependence of $\Delta\text{N}/\Delta\text{C}_2\text{H}_4$ on $(\text{N})_0$, and since the reaction $\text{N} + \text{NH} \rightarrow \text{N}_2 + \text{H}$ will not account for this dependence, regardless of the source of the NH, we prefer the catalyzed recombination route as the predominant mode of destruction of N atoms without accompanying HCN formation.

Proposed Mechanism

In view of the above discussion, we propose the following mechanism as being most consistent with our results. In order to simplify our mathematical treatment, the equations have been renumbered.



Reaction (4) is the initial source of H atoms, which then cause reactions (5-7). Reaction (7) is proposed as a plausible termination step for H atom reactions. Qualitatively it can be seen that at short reaction times and/or low ethylene input rates, provided $k_2[N]$ is of appreciable magnitude compared to k_3 , the catalyzed recombination of N atoms would predominate. At longer reaction times and/or higher ethylene input rates, however, reactions caused by H atoms become more important relative to the recombination reaction (2). These later reactions ultimately lead to HCN formation. This mechanism therefore predicts that $\Delta N/\text{HCN}$ or $\Delta N/\Delta C_2H_4$ would decrease with increasing reaction time and increasing $[C_2H_4]_0$. This has been observed by Herron.⁴⁰ Our mechanism also predicts that $\Delta N/\Delta C_2H_4$ increases with increasing initial N atom concentration, $[N]_0$, as is observed in Figures 24 and 25. This feature of the reaction is not included in Herron's mechanism. The mechanism outlined in reactions (1-7) also explains the increase in HCN yield caused by H atom addition. The effect of poisoning the system would tend to increase the importance of reaction (5) relative to the wall reaction (7) and would therefore reduce the ratio $\Delta N/\Delta C_2H_4$. This is also observed, as shown in Fig. 24.

The wall termination reaction (7) is believed to be the most important termination step when N atoms are present in excess. At high values of $[C_2H_4]_0$, radical-radical combination reactions would be expected to become important terminating processes.

If the steady state approximation is employed, it can be shown that

$$-\frac{d[N]}{dt} = 2k_1[N][C_2H_4] + 2k_5[H][C_2H_4] \quad (64)$$

(see Appendix A) and if $k_2[N] \gg k_3$, then

$$-\frac{d[C_2H_4]}{dt} \doteq k_5[H][C_2H_4] \quad (65)$$

Eliminating the reaction time as a parameter leads to

$$\frac{d[N]}{d[C_2H_4]} \doteq \frac{2k_1[N]}{k_5[H]} + 2 \quad (66)$$

The steady state concentration of H atoms is

$$\frac{1}{[H]} = \frac{k_2k_7}{2k_1k_3} \cdot \frac{1}{[C_2H_4]} - \frac{k_2k_5}{k_1k_3} \quad (67)$$

If it is further assumed that $k_7 \gg 2k_5[C_2H_4]$, then we may write

$$\frac{d[N]}{d[C_2H_4]} = \frac{k_2k_7}{k_3k_5} \cdot \frac{[N]}{[C_2H_4]} + 2 \quad (68)$$

It may also be shown (see Appendix A) that an approximate solution for this equation is given by

$$\frac{\Delta[N]}{\Delta[C_2H_4]} = \frac{k_2k_7}{k_3k_5} \cdot \frac{[N]_0}{[C_2H_4]_0} + 2 \quad (69)$$

From Fig. 25, it can be seen that our data appear to fit the empirical relationship

$$\frac{\Delta[N]}{\Delta[C_2H_4]} = A \frac{[N]_0}{[C_2H_4]_0} + B \quad (70)$$

The intercepts obtained in Figures 24 and 25 are 3.3 ± 0.5 , rather than 2, as predicted by our simplified treatment. This

may indicate that in the expansion of the integrated rate expression (Appendix A), neglect of higher order terms was not justified. It might also indicate that neglect of the reactions $N + H_{\text{wall}} \rightarrow NH$, followed by $N + NH \rightarrow N_2 + H$ is not justified, or that the assumptions $k_2[N] \gg k_3$ and $k_7 \gg 2k_5[C_2H_4]$ are oversimplifications. However, our simplified treatment does explain all of the main features of the reaction, except that the predicted intercepts for Figures 24 and 25 does not appear quite large enough. A completely rigorous treatment becomes mathematically intractable.

If the slopes of the plots in Fig.25 are multiplied by the appropriate initial ethylene concentrations, values for k_2k_7/k_3k_5 of 0.5 and 0.83 are obtained. If the plot for the poisoned system in Fig.24 is divided by $[N]_0$, a value of $k_2k_7/k_3k_5 = 0.89$ is obtained. The mean of the three values is $k_2k_7/k_3k_5 = 0.74$.

Comparison with Herron's Mechanism

The main difference between the mechanism suggested in the present work and that suggested by Herron is in the mode of N atom decay without equivalent ethylene destruction. In Herron's mechanism, this takes place via the two reaction steps



In the present work the reaction $N + (NC_2H_4) \rightarrow N_2 + C_2H_4$ serves this purpose. The latter reaction was precluded by Herron⁴⁰ and Verbeke and Winkler³⁶ since they found the ratio $\Delta N/HCN$ to be independent of $[N]_0$. Our results for ethylene destruction would

seem to indicate that this apparent constancy holds only for very high $[C_2H_4]_0$ but not for a lower value of $[C_2H_4]_0$.

We also suggest that the abstraction of an H atom from C_2H_5 by N, although it may occur to some extent, would not be the most important process for destruction of C_2H_5 at room temperature. Since the coupling reaction to form our (NC_2H_5) complex would probably have a low activation energy and since the photolysis of ethyl azide has been shown to yield to CN containing products, we suggest that, on the contrary, encounters between N and C_2H_5 may lead to HCN.

Summary

Our results of an investigation of the reactions of active nitrogen with ethylene and deuterated ethylenes may be explained by a mechanism in which a first order recombination of N atoms catalyzed by ethylene occurs. The catalyzed recombination process is decreased in importance under conditions where H atom reactions are favored.

The fact that the rate of N atom disappearance is not greater than first order in N atoms indicates

- a) if a catalyzed recombination is taking place, it proceeds via a "sticky" collision between N and C_2H_4 , such that the order with respect to N atoms is kept close to unity.
- b) initiation of the reaction by $A^3\Sigma_u^+ N_2$ appears unlikely since N in its A state is believed to result solely from the reaction $N + N + M \rightarrow N_2^* + M$ which is second order in nitrogen atoms.

A better understanding of the precise role of H atoms in the system could be obtained if the precise concentration of H atoms in the reaction zone could be monitored. An indication of the extent of H atom reactions with ethylene was obtained from the rate of conversion of C_2D_3H to C_2D_4 . Our results for the variation in distance of the hydrogen discharge from the reaction zone are inadequate for an exact determination of the dependence of $\Delta N/HCN$ on $[H]$.

The major conclusion of our work is that hydrogen cyanide formation, or its approximate equivalent, ethylene destruction, is not an accurate measure of the nitrogen atom content of active nitrogen. The last remaining bit of evidence supporting the HCN method of monitoring N atom concentrations was the work of Back and Fersht.³⁸ They believed that $A^3\Sigma_u^+ N_2$ molecules were able to compete with nitrogen atoms for reaction with nitric oxide, which resulted in the nitric oxide titration method giving apparent measures of N atom concentrations which were too high. However, since the mechanism of formation of $A^3\Sigma_u^+ N_2$ molecules now appears to be established, it is known that the steady state concentration of $A^3\Sigma_u^+ N_2$ molecules is far too low for A state molecules to be able to compete with nitrogen atoms for reaction with NO. Furthermore, our results provide an alternative explanation for the results of Back and Fersht, which is consistent with the inaccuracy of the HCN technique and the accuracy of the NO titration for measuring nitrogen atom concentrations.

Our proposed mechanism for the reaction of active nitrogen

with ethylene differs from that postulated by Herron⁴⁰ in the means of nitrogen atom destruction without formation of HCN. Our considerations have cast some doubt on the mode of NH production (which is subsequently consumed by nitrogen atoms) proposed by Herron.⁴⁰ We suggest (a) that reaction of N atoms with C_2H_5 would not primarily yield NH radicals and ethylene and the corollary (b) that if imino radicals are produced, their formation from the wall reaction of nitrogen atoms and hydrogen atoms is a more favorable source.

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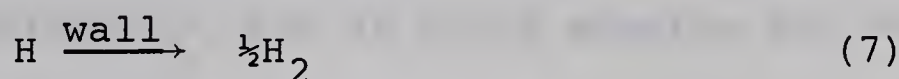
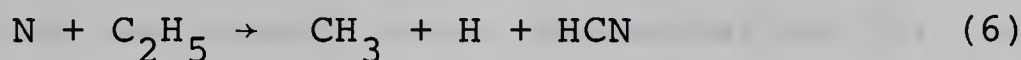
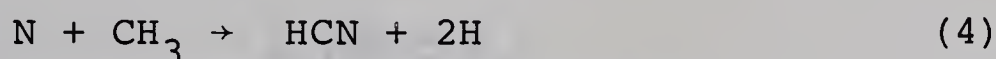
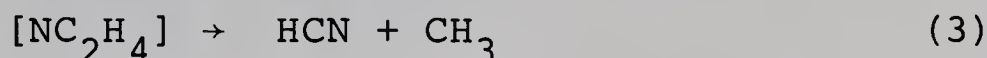
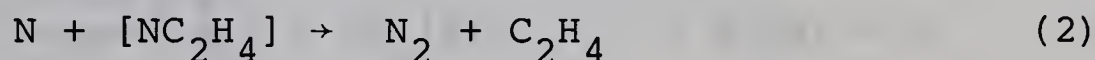
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APPENDIX A

KINETIC CALCULATIONS BASED ON THE PROPOSED MECHANISM



If the steady state approximation is valid, then

$$\frac{d[\text{NC}_2\text{H}_4]}{dt} = k_1[\text{N}][\text{C}_2\text{H}_4] - (k_2[\text{N}] + k_3)[\text{NC}_2\text{H}_4] = 0 \quad (\text{I})$$

$$\therefore [\text{NC}_2\text{H}_4] = \frac{k_1[\text{N}][\text{C}_2\text{H}_4]}{(k_2[\text{N}] + k_3)}$$

$$\text{Now, } \frac{d[\text{CH}_3]}{dt} = k_3[\text{NC}_2\text{H}_4] - k_4[\text{N}][\text{CH}_3] + k_6[\text{N}][\text{C}_2\text{H}_5] = 0 \quad (\text{II})$$

$$\frac{d[\text{H}]}{dt} = 2k_4[\text{N}][\text{CH}_3] - k_5[\text{H}][\text{C}_2\text{H}_4] + k_6[\text{N}][\text{C}_2\text{H}_5] - k_7[\text{H}] = 0 \quad (\text{III})$$

$$\frac{d[\text{C}_2\text{H}_5]}{dt} = k_5[\text{H}][\text{C}_2\text{H}_4] - k_6[\text{N}][\text{C}_2\text{H}_5] = 0 \quad (\text{IV})$$

From equation (IV) we see that equation (III) may be written

$$2k_4[\text{N}][\text{CH}_3] - k_7[\text{H}] = 0 \quad (\text{IIIa})$$

If we multiply equation (II) by two and add it to equation (IIIa),

$$\text{then } 2k_3[\text{NC}_2\text{H}_4] + 2k_6[\text{N}][\text{C}_2\text{H}_5] - k_7[\text{H}] = 0 \quad (\text{V})$$

$$\text{Since } k_3 [\text{NC}_2\text{H}_4] = k_3 \left(\frac{k_1 [\text{N}] [\text{C}_2\text{H}_4]}{k_2 [\text{N}] + k_3} \right)$$

and $k_6 [\text{N}] [\text{C}_2\text{H}_5] = k_5 [\text{H}] [\text{C}_2\text{H}_4]$, we may write

$$2k_3 \left(\frac{k_1 [\text{N}] [\text{C}_2\text{H}_4]}{k_2 [\text{N}] + k_3} \right) + 2k_5 [\text{H}] [\text{C}_2\text{H}_4] - k_7 [\text{H}] = 0 \quad (\text{Va})$$

or we may write

$$[\text{H}] = 2k_3 \frac{k_1 [\text{N}] [\text{C}_2\text{H}_4]}{(k_2 [\text{N}] + k_3) (k_7 - 2k_5 [\text{C}_2\text{H}_4])} \quad (\text{VI})$$

Rather than writing the steady state concentration for the remaining radicals individually, let us first examine the expression for the rate of N disappearance, i.e.,

$$-\frac{d[\text{N}]}{dt} = k_1 [\text{N}] [\text{C}_2\text{H}_4] + k_2 [\text{N}] [\text{NC}_2\text{H}_4] + k_4 \text{NCH}_3 + k_6 [\text{N}] [\text{C}_2\text{H}_5].$$

Using equations I, IV, IIIa, and Va, we may write

$$\begin{aligned} -\frac{d[\text{N}]}{dt} &= k_1 [\text{N}] [\text{C}_2\text{H}_4] + k_2 [\text{N}] \left(\frac{k_1 [\text{N}] [\text{C}_2\text{H}_4]}{k_2 [\text{N}] + k_3} \right) + k_3 \left(\frac{k_1 [\text{N}] [\text{C}_2\text{H}_4]}{k_2 [\text{N}] + k_3} \right) \\ &\quad + k_5 [\text{H}] [\text{C}_2\text{H}_4] + k_5 [\text{H}] [\text{C}_2\text{H}_4] \\ &= 2k_1 [\text{N}] [\text{C}_2\text{H}_4] + 2k_5 [\text{H}] [\text{C}_2\text{H}_4] \end{aligned} \quad (\text{VII})$$

The expression for the rate of disappearance of ethylene molecules is

$$\begin{aligned} -\frac{d[\text{C}_2\text{H}_4]}{dt} &= k_1 [\text{N}] [\text{C}_2\text{H}_4] - k_2 [\text{N}] [\text{NC}_2\text{H}_4] + k_5 [\text{H}] [\text{C}_2\text{H}_4] \quad (\text{VIII}) \\ &= k_1 [\text{N}] [\text{C}_2\text{H}_4] - k_2 [\text{N}] \left(\frac{k_1 [\text{N}] [\text{C}_2\text{H}_4]}{k_2 [\text{N}] + k_3} \right) + k_5 [\text{H}] [\text{C}_2\text{H}_4] \end{aligned}$$

If we employ the simplifying assumption $k_2N \gg k_3$ then

$$-\frac{d[C_2H_4]}{dt} \approx k_5[H][C_2H_4].$$

Eliminating the reaction time as a parameter,

$$\frac{d[N]}{d[C_2H_4]} \approx \frac{2k_1([N])}{k_5([H])} + 2 \quad (IX)$$

We may express equation (VI) above as

$$\frac{1}{[H]} \approx \frac{k_2k_7}{2k_1k_3} \left(\frac{1}{[C_2H_4]} \right) - \frac{k_2k_5}{k_1k_3}$$

if $k_2N \gg k_3$. If it is further assumed that $k_7 \gg 2k_5[C_2H_4]$

then

$$\frac{1}{[H]} \approx \frac{k_2k_7}{2k_1k_3} \left(\frac{1}{[C_2H_4]} \right) \quad (VIa)$$

We may therefore approximate equation (IX) by

$$\frac{d[N]}{d[C_2H_4]} \approx \frac{k_2k_7}{k_3k_5} \left(\frac{[N]}{[C_2H_4]} \right) + 2$$

Now, this is a linear differential equation of the first order and may be written as

$$\frac{dy}{dx} = K_1 \frac{y}{x} + 2$$

if we define $y = [N]$, $x = [C_2H_4]$, and $K_1 = k_2k_7/k_3k_5$. Alternatively the above may be written

$$\frac{dy}{dx} + \left[\left(-\frac{K_1}{x} \right) y - (+2) \right] = 0$$

The equation may be made exact if both members are multiplied by the integrating factor.

$$I = e^{\int P(x) dx}$$

where $P(x) = -K_1/x$. Therefore $\int P(x)dx$ is

$$\int P(x) dx = -K_1 \int \frac{dx}{x} = -K_1 \ln x$$

$$\therefore e^{\int P(x) dx} = e^{-K_1 \ln x} = x^{-K_1}$$

$$\text{Now } y e^{-\int P(x) dx} - \int Q(x) e^{\int P(x) dx} dx = C$$

Since we have $Q(x) = 2$, then

$$\frac{y}{x^{K_1}} - 2 \int \frac{dx}{x^{K_1}} = C$$

$$\therefore y x^{-K_1} - \frac{2}{(-K_1 + 1)} x^{-K_1 + 1} = C.$$

$$\therefore y = \frac{2x}{1 - K_1} + C x^{K_1}$$

$$\therefore y + \frac{2x}{K_1 - 1} = C x^{K_1}$$

Taking logarithms,

$$\ln(y + \frac{2x}{K_1 - 1}) = K_1 \ln x + \ln C$$

$$\therefore \ln(y + \frac{2x}{K_1 - 1}) - K_1 \ln x = \ln C.$$

For reaction times $t = 0$ and $t = t$ we may write

$$\ln(y + \frac{2x_t}{K_1 - 1}) - K_1 \ln x_t = \ln(y_0 + \frac{2x_0}{K_1 - 1}) - K_1 \ln x_0$$

$$\ln \left[\frac{y_t + \frac{2x_t}{K_1 - 1}}{y_0 + \frac{2x_0}{K_1 - 1}} \right] = K_1 \ln \left(\frac{x_t}{x_0} \right)$$

Expanding the logarithms as a power series and omitting higher than first order terms.

$$\frac{\left[y_t + \frac{2x_t}{K_1 - 1} \right]}{\left[y_0 + \frac{2x_0}{K_1 - 1} \right]} - 1 \approx K_1 \left(\frac{x_t}{x_0} - 1 \right).$$

$$\frac{\left[y_t + \frac{2x_t}{K_1 - 1} \right] - \left[y_0 + \frac{2x_0}{K_1 - 1} \right]}{\left[y_0 + \frac{2x_0}{K_1 - 1} \right]} = K_1 \left(\frac{x_t - x_0}{x_0} \right)$$

If we define $\Delta y = y_0 - y_t$ and $\Delta x = x_0 - x_t$, then

$$\frac{\left[\Delta y + \frac{2\Delta x}{K_1 - 1} \right]}{\left[y_0 + \frac{2x_0}{K_1 - 1} \right]} = K_1 \frac{\Delta x}{x_0}$$

$$\frac{\Delta y + \frac{2\Delta x}{K_1 - 1}}{\Delta x} = \frac{K_1}{x_0} \left[y_0 + \frac{2x_0}{K_1 - 1} \right]$$

$$\therefore \frac{\Delta y}{\Delta x} + \frac{2}{K_1 - 1} = K_1 \left(\frac{y_0}{x_0} + \frac{2}{K_1 - 1} \right).$$

$$\therefore \frac{\Delta y}{\Delta x} = K_1 \frac{y_0}{x_0} + 2$$

Therefore the differential equation

$$\frac{d[N]}{d[C_2H_4]} = \frac{k_2 k_7}{k_3 k_5} \frac{[N]}{[C_2H_4]} + 2$$

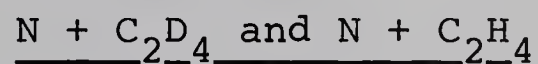
may be integrated to yield the approximate solution

$$\frac{\Delta [N]}{\Delta [C_2H_4]} = \frac{k_2 k_7}{k_3 k_5} \frac{[N]_0}{[C_2H_4]_0} + 2.$$

APPENDIX B

TABLE I

MASS SPECTRA OF THE PRODUCTS OF THE REACTIONS



P_{N₂} = 2.6 Torr Electron Beam = 20 eV

<u>m/e</u>	Relative Intensity	
	C ₂ D ₄ [*] <u>Reaction</u>	C ₂ H ₄ <u>Reaction</u>
2	-	2.8
4	10.7	-
14	1.1	1.4
15	0.6	2.0
16	1.2	3.0
17	0.9	2.5
18	0.4	-
19	1.2	-
20	4.3	-
25	-	0.6
26	7.6	5.0
27	10.6	100
28	100 (calc)	-
30	5	1.0
31	2.8	-
34	1.5	-
36	0.5	-
38	-	1.2
39	-	3.6
40	0.8	5.4
41	0.3	2.8
42	5.3	1.1
43	2.0	0.4
44	9.8	0.4
52	1.7	0.8

* These values are only approximate since they are based on a calculated peak height for m/e = 28.

TABLE 2

HCN PRODUCTION FROM THE $N + C_2H_4$ REACTION

$P_{N_2} \approx 1$ Torr

<u>C_2H_4 Input</u> <u>(μmoles/sec)</u>	<u>HCN Produced</u> <u>(μmoles/sec)</u>
1.28	0.74
1.61	1.17
2.49	1.51
3.25	1.76
5.26	2.27
6.19	2.09
9.54	2.01

TABLE 3

IONIZATION EFFICIENCY OF $m/e = 14$

$$P_{N_2} = 0.63 \text{ Torr}$$

Ion Current (% of 70 eV value)		Electron Volts (uncorrected)	Ion Current (% of 70 eV value)		Electron Volts (uncorrected)
Discharge			Discharge		
ON	OFF		ON	OFF	
0.0315	-	12.0	0.780	-	19.0
0.0430	-	12.2	0.840	-	19.5
0.0570	-	12.4	0.910	-	20.0
0.0710	-	12.6	0.980	-	20.5
0.0940	-	12.8	1.02	-	21.0
0.0990	-	13.0	NM*	0.0110	21.2
0.118	-	13.2	NM	0.0140	21.4
0.139	-	13.4	1.12	NM	21.5
0.151	-	13.6	NM	0.0195	21.6
0.171	-	13.8	NM	0.0395	21.8
0.190	-	14.0	1.24	0.0710	22.0
0.206	-	14.2	NM	0.135	22.2
0.226	-	14.4	NM	0.225	22.4
0.247	-	14.6	1.53	NM	22.5
0.271	-	14.8	NM	0.350	22.6
0.290	-	15.0	NM	0.590	22.8
0.316	-	15.2	2.06	0.800	23.0
0.337	-	15.4	NM	1.03	23.2
0.347	-	15.6	NM	1.37	23.4
0.365	-	15.8	2.80	NM	23.5
0.390	-	16.0	NM	1.66	23.6
0.410	-	16.2	NM	2.02	23.8
0.420	-	16.4	3.75	2.35	24.0
0.450	-	16.6	NM	2.75	24.2
0.465	-	16.8	NM	3.20	24.4
0.490	-	17.0	4.50	NM	24.5
0.525	-	17.2	NM	3.55	24.6
0.550	-	17.4	NM	3.95	24.8
0.570	-	17.6	5.60	4.40	25.0
0.590	-	17.8	6.80	5.50	25.5
0.620	-	18.0	8.00	6.80	26.0
0.710	-	18.5			

* NM -. not measured

TABLE 4

RELATION BETWEEN ION CURRENT AT $m/e = 14$ AND AFTERGLOW INTENSITY

$$P_{N_2} = 0.63 \text{ Torr}$$

<u>Ion Current (IC)</u> <u>(arbitrary units)</u>	$(IC)^2$ $\times 10^{-3}$ <u>(arbitrary units)²</u>	<u>Afterglow Intensity</u> <u>(arbitrary units)</u>
66	4.34	4.5
85	7.20	7.5
112	12.5	10.5
127	16.1	13.0
140	19.6	15.5
146	21.3	17.0
155	24.0	19.0
161	25.9	21.0

TABLE 5

RATE OF DECAY OF NITROGEN ATOMS

IN THE PRESENCE OF VARIOUS INITIAL CONCENTRATIONS OF C_2D_4

Initial atom concentration $[N]_0 = 10.2 \times 10^{13}$ atoms/cc

Total pressure = 0.63 Torr

$[N]$, atoms/cc, $\times 10^{-13}$

Reaction time

millisec

for various initial concentrations of C_2D_4

$[C_2D_4]_0 = 2.5_8 \times 10^{13} \quad 6.75 \times 10^{13} \quad 15.3 \times 10^{13} \quad 28.9 \times 10^{13}$

2.3 ₇	6.5 ₈	5.5 ₆	4.8 ₄	4.7 ₄
3.5 ₅	6.5 ₃	5.7 ₆	4.2 ₃	3.6 ₂
4.7 ₄	5.9 ₆	5.0 ₀	4.0 ₈	3.2 ₁
6.8 ₁	5.7 ₁	4.6 ₉	3.6 ₂	2.6 ₀
9.4 ₈	6.1 ₂	4.5 ₉	3.3 ₇	2.1 ₉
14.2	5.5 ₆	4.2 ₃	2.7 ₅	1.4 ₃
19.0	5.4 ₆	3.9 ₈	2.2 ₉	0.8 ₂
26.1	5.4 ₆	3.5 ₇	2.0 ₉	0.6 ₁
30.8	5.2 ₀	3.5 ₂	1.6 ₃	0.2 ₆

TABLE 6

CONCENTRATION OF NITROGEN ATOMS AS A FUNCTION OF
INITIAL CONCENTRATION OF C₂D₄ FOR VARIOUS REACTION TIMES

Initial concentration of atomic nitrogen

$[N]_0 = 8.6 \times 10^{13}$ atoms/cc. Total pressure = 0.63 torr.

All concentrations are in $\times 10^{13}$ molecules/cc.

t = 7.1 millisec		t = 26.7 millisec	
[N]	[C ₂ D ₄] ₀	[N]	[C ₂ D ₄] ₀
5.70	4.18	4.73	4.83
5.02	6.44	3.93	7.40
4.22	9.66	3.57	8.70
3.70	14.5	2.77	11.3
3.22	19.6	2.54	13.5
2.71	27.0	1.93	16.7
		1.13	21.8
2.16	36.4	0.52	29.9
1.67	47.3	0.23	39.6
t = 14.2 millisec		t = 37.7 millisec	
[N]	[C ₂ D ₄] ₀	[N]	[C ₂ D ₄] ₀
4.57	6.44	5.41	2.90
4.22	7.40	3.64	4.83
3.84	9.66	3.29	5.80
3.54	11.3	2.67	7.40
3.16	14.5	2.19	8.70
2.90	16.4	1.51	11.3
2.42	19.6	1.16	13.5
1.74	27.4	0.74	17.1
1.16	36.4	0.32	21.5
0.77	47.3		

TABLE 7

RATE OF DECAY OF NITROGEN ATOMS

FOR TWO DIFFERENT INITIAL CONCENTRATIONS OF C_2D_4

Initial nitrogen atom concentration

$[N]_0 = 10.8 \times 10^{13}$ atoms/cc. Total pressure = 2.6 torr.

Reaction time millisec	$[N], \text{ atoms/cc, } \times 10^{-13}$		
	for different initial concentrations of C_2D_4 $[C_2D_4]_0 = 13.6 \times 10^{13} \quad 31.4 \times 10^{13}$		
3.7 ₅	8.9 ₂		8.1 ₄
4.5 ₀	8.4 ₃		7.4 ₉
6.0 ₁	7.9 ₂		6.2 ₇
7.5 ₁	7.4 ₂		5.2 ₆
9.0 ₂	6.9 ₇		4.1 ₁
10.5	6.5 ₅		3.0 ₉
12.0	5.9 ₈		2.3 ₁
13.5	5.6 ₉		1.9 ₄
15.8	5.4 ₇		
17.8			1.0 ₈

TABLE 8

DEPENDENCE OF REAGENT CONCENTRATION ON $[C_2D_3H]_0$

$$\frac{AT}{P_{N_2}} = 2.6 \text{ TORR}$$

All concentrations are in $\times 10^{13}$ molecules/cc

A "Unpoisoned" System

[N]	$\Delta [C_2D_3H]$	$[C_2D_4]$ Formed	$[C_2D_3H]_0$
72	-	-	-
57.5	1.00	-	6.3
43.5	2.40	-	9.7
31.0	5.00	0.20	14.3
8.5	11.00	0.66	26.5
6.0	13.2	1.00	32.1
0.5	17.6	1.76	50.3

B "Poisoned" System

[N]	$\Delta [C_2D_3H]$	$[C_2D_4]$ Formed	$[C_2D_3H]_0$
72	-	-	-
51	1.50	-	5.2
46	2.40	-	6.5
39	3.22	0.07	8.7
27.5	5.80	0.16	13.1
16.5	9.00	0.32	18.2
8.5	10.3	0.52	24.6
5.0	14.2	0.90	31.0
2.0	16.1	1.32	40.0
0.5	18.9	2.03	60.2

TABLE 9

CHANGE IN HCN PRODUCTION DUE TO H ATOM ADDITION AS A FUNCTION OF THE
DISTANCE FROM THE HYDROGEN INLET TO THE REACTANT INLET UPSTREAM

$P_{N_2} \approx 3$ Torr

HCN Production*		Δ HCN	Distance
<u>(arbitrary units)</u>		<u>(% of value with H Discharge OFF)</u>	<u>(cm)</u>
H Discharge OFF	H Discharge ON		
45	94	109	0
61	125	105	1
55	107	94.6	2
59	103	74.7	3
48	82	70.8	4
64	95	48.4	5
66	95	43.9	6
71	99	39.5	7

* corrected for the contribution of $C_2H_3^+$ to the ion current at $m/e = 27$

TABLE 10

CHANGE IN HCN PRODUCTION DUE TO H ATOM ADDITION
AS A FUNCTION OF THE DISTANCE BETWEEN
THE REACTION ZONE AND THE HYDROGEN DISCHARGE

$P_{N_2} \approx 3$ Torr

HCN Production*		Δ HCN	Distance
<u>(arbitrary units)</u>		<u>(% of 'OFF' value)</u>	<u>(cm)</u>
H Discharge OFF	H Discharge ON		
60	113	88.4	2.5
60	112	86.7	3.0
60	107	78.3	6.5
60	100	66.7	10.8
60	86	43.3	14.5
60	80	33.3	21.3
60	77	28.3	27.3

* corrected for the contribution of $C_2H_3^+$ to the ion current at $m/e = 27$

TABLE 11

CHANGE IN HCN PRODUCTION DUE TO H ATOM ADDITION
AS A FUNCTION OF THE $[C_2H_4]_0$

$P_{N_2} \approx 3$ Torr

HCN Production*		$[C_2H_4]_0$
<u>(arbitrary units)</u>		<u>(arbitrary units)</u>
H Discharge OFF	H Discharge ON	
36	71	25
49	88	37
62	87	54
69	89	78
76	88	161
72	90	224

* corrected for the contribution of $C_2H_3^+$ to the ion current at $m/e = 27$

TABLE 12

APPARENT SECOND ORDER SPECIFIC RATE CONSTANTS, k_{app} (cc. molecule⁻¹sec⁻¹) FOR THE DISAPPEARANCE OF NITROGEN ATOMS IN THE PRESENCE OF ETHYLENE, IN cc.molecule⁻¹sec⁻¹.

A $[N]_0 = 10.2 \times 10^{13}$ atoms/cc $P_{N_2} = 0.63$ Torr

$[C_2D_4]_0$	k_{app}
2.6×10^{13} molecules/cc	2.1×10^{-13}
6.8×10^{13} "	2.0×10^{-13}
15.3×10^{13} "	2.2×10^{-13}
28.7×10^{13} "	3.0×10^{-13}

B $[N]_0 = 8.6 \times 10^{13}$ atoms/cc with C_2D_4 $P_{N_2} = 0.63$ Torr

t msec	k_{app}
7.1	3.5×10^{-13}
14.2	3.2×10^{-13}
26.7	3.2×10^{-13}
37.7	3.2×10^{-13}

C $[N]_0 = 10.8 \times 10^{13}$ atoms/cc $P_{N_2} = 2.6$ Torr

$[C_2D_4]_0$	k_{app}
13.6×10^{13} molecules/cc	3.5×10^{-13}
31.4×10^{13} "	5.1×10^{-13}

D $[N]_0 = 72 \times 10^{13}$ atoms/cc $P_{N_2} = 2.6$ Torr
t = 21.2 msec

	k_{app}
"Poisoned" system	4.4×10^{-13}
"Unpoisoned" system	4.4×10^{-13}

TABLE 13

DEPENDENCE OF N ATOMS DESTROYED/ETHYLENE MOLECULES DESTROYED
RATIO ON INITIAL N ATOM CONCENTRATION AT TWO DIFFERENT $[C_2D_4]_0$

Concentrations are in $\times 10^{13}$ molecules/cc.

$$P_{N_2} = 2.6 \text{ Torr}$$

A) $[C_2D_4]_0 = 7.1 \times 10^{13}$ molecules/cc.

<u>[N]</u>	<u>$\Delta [N]$</u>	<u>$\Delta [C_2D_4]$</u>	<u>$\Delta [N] / \Delta [C_2D_4]$</u>
34	23	4.1	5.6
66	41	4.8	8.6
80	48	5.0	9.5
92	53	5.2	10.2
103	57	5.3	10.8
119	64	5.5	11.7
131	72	5.6	12.9

B) $[C_2D_4]_0 = 34.6 \times 10^{13}$ molecules/cc.

<u>[N]</u>	<u>$\Delta [N]$</u>	<u>$\Delta [C_2D_4]$</u>	<u>$\Delta [N] / \Delta [C_2D_4]$</u>
40	40	8.6	4.6
50	50	10.0	5.0
60	60	11.2	5.3
75	75	13.4	5.6
90	90	15.0	6.0
113	113	17.4	6.5
132	132	19.2	6.9

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